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# THE OPTICAL ANISOTROPY AND HETEROGENEITY OF VITREOUS SILICA

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Received March 13, 1950

## 1. Introduction

Vitreous silica is a remarkable and most useful material and the investigation of its structure and properties is therefore of much interest. As it is an amorphous solid, one would naturally expect its optical behaviour to be that of an isotropic medium. Actually, however, a polished plate of vitreous silica when interposed in the path of a beam of light between a polariser and an analyser set in the position for extinction always gives rise to an observable restoration of light, as was remarked long ago by Rayleigh (1920). A characteristic feature of the phenomenon is that the restoration of light is not uniform over the surface of the plate. This effect is particularly striking in the case of the disks of the so-called optical silica which are built up by a special process. These exhibit a birefringence pattern of concentric circles, evidently connected with the way in which the material had been fabricated (Fig. 10 in Plate IX).

The present paper describes the results of a re-examination of the behaviour of vitreous silica referred to above, undertaken with a view to elucidate the nature and origin of the phenomenon. The material available for the study included several specimens of the silica glass collected by Dr. L. J. Spencer in the Sand Sea of the Libyan desert in December 1934 and very generously presented to the author during a visit to his London home in 1948. The examination of the specimens of this naturally occurring substance has yielded highly significant results. Numerous examples of the commercially available material have also been examined. These included circular discs of different thicknesses and diameters, two belonging to this Institute and several others very kindly loaned for the study by Prof. R. S. Krishnan. Two silica rods with different forms of cross-section which were presented to the author by Messrs. Adair Dutt of Madras have also been studied.

Large Nicols, such as those used by Rayleigh in his investigation, were not available. But polaroids three inches square in area serve the same purpose admirably. Except in the case of disks having polished faces, it is useful and indeed generally necessary to immerse the specimen under study in a flat-sided trough filled with xylene or carbon tetrachloride. The use of a light source of adequate intensity is essential. Indeed, the most

satisfactory way of examining any specimen is to view it when traversed by a direct beam of sunlight with the arrangements described above.

Since the optical anisotropy exhibited by vitreous silica exhibits local variations, it follows that the material is optically heterogeneous. This may be readily demonstrated without the use of polarised light by merely holding a polished disk of vitreous silica in the path of a beam of light diverging from a brilliant source of light of small area. The light which has traversed the disk when received on a screen placed at a suitable distance is found to exhibit a pattern of light and shade bearing a recognisable relationship to the features exhibited by the same specimen between crossed polaroids.

## 2. Observations with Natural Silica Glass

A remarkable occurrence of vitreous silica scattered over an extensive area in the Libyan desert was reported in a paper by Clayton and Spencer (1934). Further details appeared in a later memoir by Spencer (1939). The material has a pale greenish-yellow colour and some of the specimens are clear and transparent. Chemical analysis shows the mineral to be nearly pure silica, $SiO_2$ making up 97½% while the rest consists of various metallic oxides. The five specimens gifted to the author by Dr. Spencer from his collection are fully representative of the Libyan occurrence and show the various characters described and illustrated in the paper by Clayton and Spencer. Two of them, though interesting in themselves, contain numerous inclusions and are therefore not suited for the present investigation. The three others when immersed in a trough containing xylene or carbon tetrachloride and placed between crossed polaroids exhibit some striking effects which are illustrated in Figs. 1, 2 and 5 of Plate VIII. Streaks or sheets of luminosity are observed traversing the interior of the glass: there are several such in each specimen, and they run parallel to each other in a direction coinciding more or less exactly with that of the longest dimension of the piece. The luminosity attains its maximum intensity when the specimen is so set that the bright streaks or sheets bisect the angle between the principal planes of the two polaroids. As is to be expected in these circumstances, they disappear when set so as to lie in either of these two planes, the whole of the specimen then appearing more or less perfectly dark.

The photographs reproduced as Figs. 1, 2 and 5 in Plate VIII were recorded with the specimen in each case set so that the luminous streaks or sheets are of maximum intensity: they are seen in the figures running diagonally. The effect was particularly conspicuous with the specimen represented in Fig. 5 which was very clear and transparent: the trough used was unfortunately not large enough to hold the entire piece, otherwise the effects would

have shown up much better in the photograph. The specimens illustrated in Figs. 1 and 2 in Plate VIII are distinctly cloudy but nevertheless show the phenomenon clearly enough.

### 3. Observations with Transparent Silica Rods

The two rods studied are shown diagrammatically as Figs. 1 and 2 below in the text. The rod illustrated in Fig. 1 has a cylindrical cross-section with a flange added at one end as shown. The second rod has a flattened cross-section and is bent in its own plane into a curve towards the end as shown in Fig. 2.

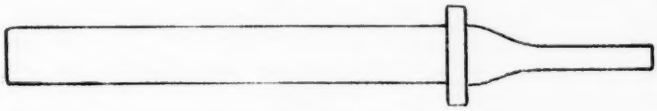

Fig. 1

Fig. 2

Examination of the cylindrical rod when immersed in carbon tetrachloride and placed between crossed polaroids shows a birefringence pattern exhibiting a great number of lines or fibres running more or less exactly parallel to the axis of the rod (Fig. 8 in Plate IX). This effect is most conspicuous when the axis of the rod is inclined at 45° to the planes of vibration of the two polaroids and vanishes completely when it is set parallel to either of these planes. In the vicinity of the flange and up to some distance on either side of it, however, a different effect is simultaneously observed. This is of much greater intensity and may be isolated by setting the rod either vertical or horizontal; the fibrous structure then ceases to be visible and the restoration of light shows the continous variation of intensity characteristic of a photoelastic pattern. The second effect thus evidently arises from a distribution of permanent stresses existing in the vicinity of the flange. When, however, the rod is set in an inclined position, both types of birefringence—structual as well as stress-optical—appear simultaneously, and they are superposed on each other. Some very curious features are observed when a fibre-line crosses a dark band of the stress-optical pattern.

The bent rod illustrated in Fig. 2 also exhibits a structural birefringence pattern, consisting of fine fibres running parallel to the axis of the rod and

bending round towards the end so as to follow its curvature. There are indications that there exists simultaneously a stress-optical birefringence, as the result of the superposition of which the structural birefringence is seen more weakly at some parts of the cross-section than at others. A similar effect is also apparent in the case of the cylindrical rod (Fig. 8 in Plate IX).

### 4. Observations with Transparent Silica Disks

Reference has already been made above to the behaviour of disks of the so-called "optical silica" built up in a particular manner which show a birefringence pattern consisting of concentric circles. The behaviour of one such disk, 4 centimetres in diameter and 8 millimetres thick, when viewed normally to itself between crossed polaroids, is illustrated in Fig. 10, Plate IX. It will be noticed that the black cross seen in the pattern cutting across the circular rings is somewhat distorted in the vicinity of the centre; when the disk is rotated in its own plane, the cross shifts about a little, showing that the structure giving rise to the observed pattern is not perfectly centro-symmetric. The disk may also be viewed *edgewise* along a diameter, its plane making any desired angle with the principal planes of the polaroids: the restoration of light then observed is very feeble if the plane of the disk is set parallel to either of them, and quite strong if set at an angle of 45° with either of them. We shall return later to the question of the interpretation of the effects observed with this disk, but will here draw attention to a remarkable feature observed in Fig. 10 in Plate IX, namely the sharp definition of the boundaries between the dark and bright areas in the pattern.

Two other disks included in the present study also show a black cross when viewed normally between crossed polaroids, but they are of the so-called "ordinary" silica, and the observed characters of the birefringence are quite different (see Fig. 6 in Plate VIII, and Fig. 12 in Plate IX). In both of these cases, the field of light in the space between the arms of the black cross consists of a criss-cross pattern of streaks intersecting each other: the general directions of the two set of streaks are respectively along the two diagonals making an angle of 45° with the arms of the black cross, as is particularly clear in Fig. 6, Plate VIII, but not so clear in Fig. 12 in Plate IX, the black cross being also a little hazy in that figure.

Figs. 7, 9 and 11 in Plate IX reproduce photographs of still another disk viewed normally to itself between crossed polaroids, the three figures representing three different settings of the disk *in its own plane*. It will be noticed that this disk does not exhibit a black cross, and that its appearance is altogether different in the three settings. In Fig. 7, we see that the streaks seen on the disk run only along one diagonal, in Fig. 9 they run only along

the other diagonal, while in Fig. 11 a few patches appear exhibiting a criss-cross pattern with streaks running along both diagonals and intersecting each other. The remarkable difference between the behaviour of this disk and those of the two others—which show a black cross and a criss-cross pattern of streaks all over in every setting—is evidently related to the fact that it is a thin disk, being only 2 millimetres thick, while the other two disks are 13 millimetres and 4 millimetres thick respectively. This explanation is supported by the results of an examination of the thickest of the three disks *viewed edgewise along a diameter*. Such examination immediately reveals in it the presence of a great many birefringent streaks parallel to the surface of the disk (Fig. 4 in Plate VIII): these are equally conspicuous in all settings of the disk in its own plane, and thus effectively form birefringent layers or sheets within the disk parallel to its faces. They appear most brilliantly when the plane of the disk is set at 45° to the principal planes of the polaroids, but continue to be visible over a very considerable range of settings of the disk on either side of this position and disappear only when the disk is parallel to one or other of the two planes. In the latter position, streaks may be seen running in directions inclined to the surface of the disk, but they are much fainter (see Fig. 3 in Plate VIII).

In Fig. 6, Plate VIII, one notices that towards the edge of this disk, the criss-cross structure of the birefringence is apparently replaced by a somewhat brighter continuum. The explanation of this effect has been investigated by immersing the disk in a trough of liquid and viewing it *edgewise* between crossed polaroids. Such an examination revealed that the structure of the disk is effectively modified near the cylindrical edge by the fire-polishing to which the latter had apparently been submitted. A feeble photo-elastic birefringence is also visible near the edges by reason of the disk having been sawn through to form its faces. The other two disks do not show this effect: they have polished faces and ground edges.

## 5. Interpretation of the Facts

Before we proceed to consider the explanation of the facts brought to light by the present investigation, it may be useful briefly to comment on the opinions expressed by Rayleigh regarding the nature of the effects noticed by him. From certain evidence detailed in his paper, he came to the conclusion that the birefringence pattern of concentric circles shown by the built-up silica disks was a stress-optical phenomenon. On the other hand, the birefringence exhibited by the silica disks of the ordinary variety was ascribed by him to a crystalline granular structure of the vitreous silica which he thought might have been derived from the quartz from which it is obtained

by fusion. He believed also that when the silica is fused and drawn out into rods, these same crystalline granules persist but are elongated into fibres.

With regard to the above-mentioned suggestions of Rayleigh, we may remark that theoretical considerations make it extremely difficult to accept them as probable or even possible. As is well known, the formation of vitreous silica from crystalline quartz is attended by a notable diminution in density from 2·65 to 2·20, and is accompanied by a sharp drop of the refractive index to 1·458 for vitreous silica from the much higher values 1·544–1·553 characteristic of quartz. There is simultaneously a fundamental change in structure, as is shown directly by X-ray studies, and is indicated also by the remarkable changes in physical properties, notably the drop in the thermal expansion coefficient from $34 \times 10^{-6}$ to $1 \cdot 3 \times 10^{-6}$. Moreover, in the range of temperature 1470°–1710° immediately preceding that of fusion, the stable crystalline form of silica is not quartz but high-cristobalite, which is an optically isotropic material. It is also known that when vitreous silica devitrifies, the product is not quartz but cristobalite. In view of all these facts, one could scarcely suppose that any trace either of the crystalline structure or of the birefringence of quartz could survive in the molten liquid obtained by its fusion and be carried over to the glass formed on solidification.

We may also remark that it was the criss-cross structure of the birefringence patterns exhibited by fairly thick disks of the ordinary silica which led Rayleigh to his hypothesis of a granular structure for vitreous silica in the mass. Actually, however, as shown by the present investigation, patterns of this type represent merely the integrated optical effect of the passage of the light through the many birefringent layers present in a thick disk. Figs. 7 and 9 in Plate IX show that even in a disk 2 millimeters thick, the birefringence pattern takes the form of elongated streaks and *not* of a criss-cross pattern. The facts of observation thus lend no support to the postulated existence of crystalline granules having an average dimension of half millimetre in vitreous silica.

We are thus forced to seek for an alternative explanation of the observed phenomena. It is useful to consider the problem in two stages. The first is the purely phenomenological approach to the facts. The various observations described in the present paper make it perfectly clear that in vitreous silica, two kinds of "accidental birefringence" are possible. The first kind is the well-known type of birefringence which is observed in a stressed isotropic solid. If such birefringence is observed in a specimen not subjected externally to any stress, we have necessarily to assume that it arises from an internally

compensated system of stresses. How such stresses are set up and persist is a question the answer to which depends on the previous thermal and mechanical history of the specimen. It may be remarked that the thermal expansion coefficient of vitreous silica is extremely small even at high temperatures. From this, it follows, and indeed is actually the case, that the photo-elastic effects arising from an unequal heating of a specimen would be small. One may therefore reasonably assume that though stresses arising from "imperfect annealing" may arise in vitreous silica, as in other types of glass, they would not be so large as to overshadow any other possible kind of effect. This leads us naturally to the recognition of a second kind of "accidental birefringence" in vitreous silca—and presumably therefore also in other amorphous solids—of a "structural birefringence" also arising from the previous thermal and mechanical history of the specimen. The distinction between this and the other is indicated by its name, *viz.*, that we are concerned *not* with the elastic deformations of an isotropic medium and the optical consequences thereof, but with changes of the ultimate structure of the substance itself resulting in its becoming birefringent. Accepting such a possibility, we see at once that the phenomena brought to light by the present investigation, both in natural silica glass and in the material prepared artificially, find a natural explanation. Indeed it would be difficult to find any other explanation, since their general character definitely excludes an interpretation of them as stress-optical birefringence of the familiar variety.

### 6. Origin of the Structural Birefringence in Vitreous Silica

As is well known, viscous liquids when stirred exhibit a temporary birefringence which disappears more or less quickly with time. A theory of this phenomena connecting it with the linear dimensions and optical characters of the molecules of the fluid and with its viscosity was given long ago by the present writer and K. S. Krishnan (1928). The case of vitreous silica is rather different from that of the organic compounds with discrete molecules considered in that paper. We may indeed recognize the presence in vitreous silica of a fundamental building unit, *viz.*, a silicon atom surrounded tetrahedrally by four oxygen atoms. But such a unit cannot be regarded as capable of moving or rotating independently of the neighbouring units of the same kind. Indeed, in the solid, the units would be firmly bound to each other at the corners by the sharing of the oxygen atoms. Free mobility of the units in the molten or liquid state would require the breaking and reforming of vast arrays of such bonds. It is this circumstance which distinguishes the behaviour of vitreous silica in the fluid state from that of ordinary liquids composed of discrete molecules bound to each other by comparatively weak forces. Given sufficient time and favourable

circumstances, one may expect to find that in the molten silica the building units link themselves in such manner as to become effectively an optically isotropic structure. Such a liquid on solidification would be optically non-birefringent. But that in any actual set of circumstances, and especially when the molten liquid is subject to any type of mechanical disturbance, it is unlikely that such an ideal state would be actually reached or that it would be exhibited in the finally resulting glass. The fashioning of a glass necessarily involves the manipulation of the material in a semi-molten state into the particular form desired. Any such operation would necessarily bring into action the tendency of the bonds connecting the silicon atoms with the oxygen atoms to resist disruption, and for the units to take up new positions by shifting the directions of the bonds rather than by their disruption and reformation. The formation of optically birefringent streaks or sheets in the medium would be a natural consequence.

The foregoing is of course only a general and qualitative picture. But it appears to afford a reasonable explanation of the special type of irregular or accidental birefringence of an obviously structural character exhibited by vitreous silica, and especially of the relationship between the optical characters of the birefringence and the geometric form of the specimen under examination which emerges from the actual facts of observation.

The photographs accompanying this paper were obtained by Mr. J. Padmanabhan, whose efficient assistance I have much pleasure in acknowledging.

## Summary

The paper describes the birefringence exhibited by vitreous silica, both in the naturally occurring material found in the Libyan desert and in the commercially available material in the forms of rods and disks. The facts revealed by the investigation are discussed. It is shown that Rayleigh's belief that vitreous silica in the mass has a crystalline granular structure cannot be sustained. It is shown further that, besides the familiar stress-optical birefringence, a second kind of effect, *viz.*, " structural birefringence " is also possible in amorphous solids and that this is particularly prominent in vitreous silica for reasons which are discussed.

12 photographs illustrate the paper.

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(*In Chronological Order*)

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Raman and Krishnan .. *Phil. Mag.*, 1928, **5**, 769.
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Spencer .. *Ibid.*, 1939, **25**, 432.

FIG. 1

FIG. 2

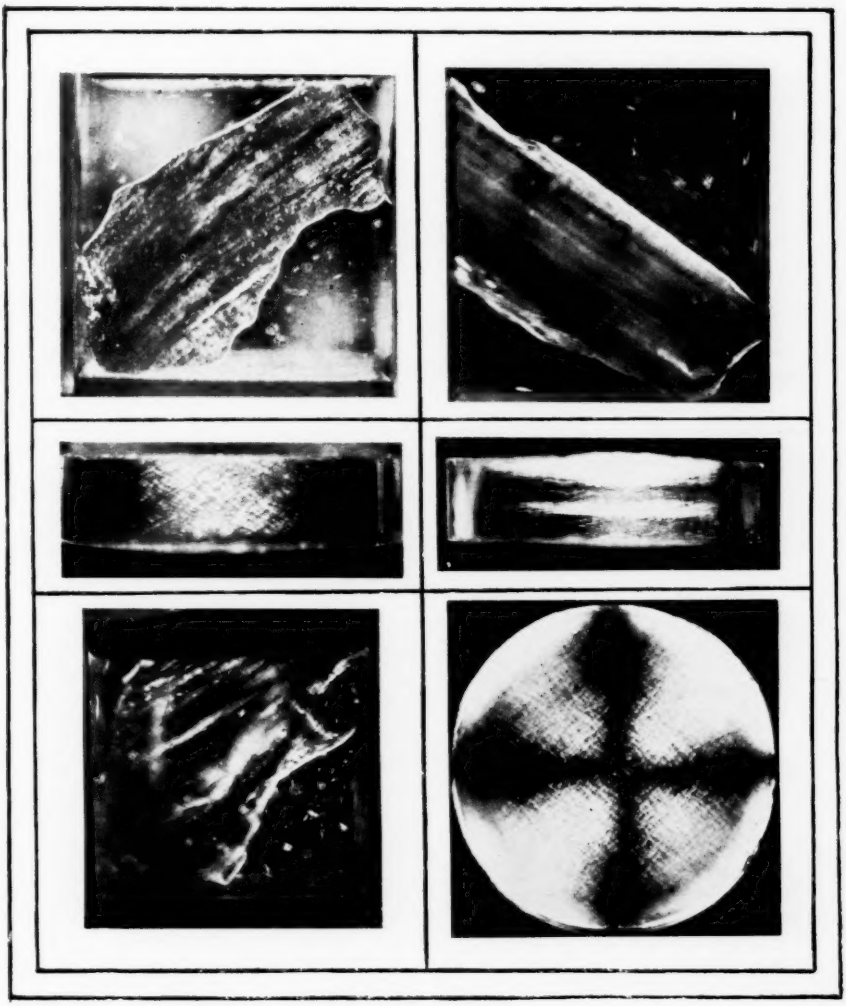

FIG. 3

FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

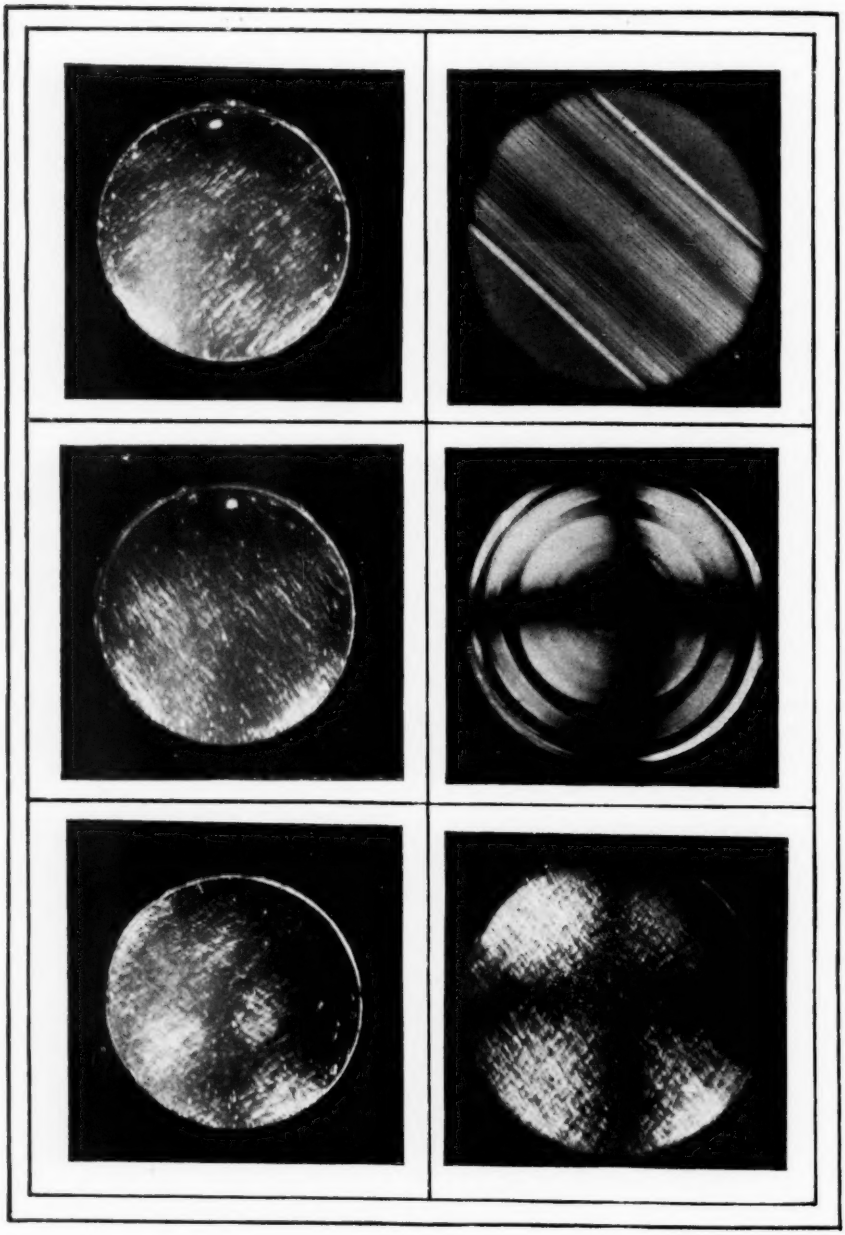

FIG. 9

FIG. 10

FIG. 11

FIG. 12

# THE MAGNETO-OPTIC ANOMALY OF ELECTROLYTES IN AQUEOUS SOLUTION

## I. Alkali Halides

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(Communicated by Prof. R. S. Krishnan, F.A.SC.)

### 1. Introduction

Recent measurements by the author (1947, 1948) of the Faraday rotation in cubic crystals for wave-lengths in the visible region have shown that the Verdet constant of most cubic crystals could well be expressed by the modified Becquerel formula (Darwin and Watson, 1927)

$$V = \gamma \frac{e}{2mc^2} \lambda \frac{dn}{d\lambda}$$

where $dn/d\lambda$ is the dispersion of the substance and $\gamma$ is a constant called the magneto-optic anomaly. These studies have indicated that the magneto-optic anomaly is very intimately connected with the nature of the binding between atoms or ions. A determination of the magneto-optic anomaly in electrolytic solutions, where the ions are comparatively free, would therefore be invaluable in the understanding of the results obtained with crystals.

Very little systematic work has been done so far on the Faraday rotation of ionic solutions. Moreover, all the investigators on this subject [Jahn (1891), Anderson and Asmussen (1932), Okazaki (1934) and de Mallemann (1942)] have only measured the magnetic rotation of solutions and not their dispersions and as such no data for the magneto-optic anomaly for solutions are available. It was with a view of filling up this gap in the literature that this series of investigations was undertaken by the author. Further, it has been shown from theoretical considerations (Rosenfeld, 1930) that the value of $\gamma$ for atoms having the inert gas structure is unity. It is therefore of some interest to find out how far this is true in the case of alkali metal ions and halogen ions which have the inert gas configuration.

This paper reports the measurement of the Faraday rotation and the dispersion of seventeen univalent halide solutions and from these the magneto-optic anomaly of the solutions have been evaluated. The rotations and values of $\gamma$ for the free ions have also been estimated. It is found that the magneto-optic anomaly of ions having the inert gas configuration is very nearly the theoretical value of one.

## 2. Experimental Methods

The apparatus that was used in these experiments has already been described (Ramaseshan, 1946; 1947). The source of light was an intense mercury arc with a Zeiss filter for separating out the $\lambda$ 5461 radiation. The light after passing through a double field polariser went through a longitudinal hole in the pole pieces of a Rutherford magnet and was received by an analyser. The analyser could measure rotations upto 0·01°.

The solutions to be studied were placed in between the two pole pieces. Two identical cells with glass end pieces of the same thickness were made. When both the cells were filled with pure water their magnetic rotations in the same field did not vary by more than 1 in 2,000. One of the cells was filled with pure double distilled water and the other with the solution. By a simple sliding arrangement the two cells could be brought between the pole pieces alternately, the two occupying exactly the same position. This arrangement removes any errors that may arise due to the non-uniformity of the field. For any current flowing through the magnet the rotations for the water and the solution were consecutively measured. This avoids errors due to fluctuations in the mains voltage. The measurements were made at room temperature which was about 25° C.

The solutions were prepared from Kahlbaum's or Merck's purest analytical reagents. A 4-molar solution was accurately prepared. The density of the solution was measured with a specific gravity bottle.

The refractive indices of the solutions were measured for $\lambda$ 5893 (Na), $\lambda$ 5461 (Hg) and $\lambda$ 4358 (Hg) by means of Pulfrich refractometer. A special water circulating arrangement kept the temperature constant during the course of the measurement. The values of the refractive index are accurate to one unit in the fourth place of decimals and the values of the dispersions are accurate to two units in the fifth place.

## 3. Methods of Calculation and Results

The specific rotations of the ions in solution are evaluated from the simple Verdet rule (1858)

$$[V_s] = [V_i]\, x_1 + [V_\omega]\, x_2,$$

where $[V_s]$, $[V_i]$ and $[V_\omega]$ are the specific rotations of the solution, the ions in solution and water, $x_1$ and $x_2$ are the number of grams of salt and water in 100 *grams of solution*. The specific rotation is defined as $[V] = V/d$, where V is the Verdet constant and $d$ is the density of the substance. The molecular rotation is $[V]_M = MV/d$, where M is the molecular weight of the

substance. The magneto-optic anomaly $\gamma$ for any solution is calculated from the modified Becquerel formula.

The magnetic rotations of the solutions were measured for $\lambda$ 5461 with water as the standard substance. The absolute value of the Verdet constant for $\lambda$ 5461 for water has been taken as 0·01547′ per cm. per oersted at 25° C. (Rodger and Watson, 1896).

Tables I–VII give the optical and the magneto-optic constants for water and the different alkali halide solutions. In these M is the molecular weight, $X_1$ and $X_2$ give the number of grams of salt and water in *100 c.cs. of solution*, $d$ the density, $n$ the refractive index and $\Delta n = n_{5893} - n_{4358}$, $V_{5461}$ the Verdet constant of the solution, $[V_i]_M$ the molecular rotation of ions in solution calculated from the Verdet mixture rule and $\gamma$ is the magneto-optic anomaly for the solutions. The value of $\frac{9n}{(n^2+2)^2}$ for each solution has also been included in the tables. These values will be made use of in the calculation of the value of $\gamma$ for the individual ions.

TABLE I

*The optical and magneto-optic constants for water*

| $n_{5893}$ | $n_{5461}$ | $n_{4358}$ | $\Delta n \times 10^5$ | $V_{5461}$ | $100\gamma$ |
|---|---|---|---|---|---|
| 1·33239 | 1·33381 | 1·33953 | 714 | 0·01547 | 76 |

TABLE II

*The magneto-optic data for univalent chloride solutions*
(4 *Normal*)

| | M | $X_1$ | $X_2$ | $d$ | $V_{5461} \times 10^3$ | $[V_i]_M \times 10$ | $100\gamma$ |
|---|---|---|---|---|---|---|---|
| HCl .. | 36·46 | 14·60 | 92·16 | 1·0674 | 19·30′ | 12·61′ | 77·8 |
| LiCl .. | 42·40 | 16·99 | 92·13 | 1·0909 | 19·49′ | 13·10′ | 79·6 |
| NaCl .. | 58·46 | 23·38 | 91·91 | 1·1529 | 20·02′ | 14·50′ | 81·4 |
| KCl .. | 74·56 | 29·86* | 87·68 | 1·1750 | 19·74′ | 15·45′ | 81·1 |
| CSCl .. | 120·94 | 48·31 | 85·67 | 1·3404 | 19·93′ | 16·70′ | 81·5 |
| RbCl .. | 168·37 | 67·37 | 83·02 | 1·5036 | 20·77′ | 19·82′ | 80·8 |
| $NH_4Cl$ .. | 53·50 | 21·42 | 84·32 | 1·0572 | 19·73′ | 16·72′ | 79·6 |

* Super saturated solution.

TABLE III

*The optical data for univalent chlorides in solutions*
(4 *Normal*)

| | $n_{5893}$ | $n_{5461}$ | $n_{4358}$ | $\Delta n \times 10^5$ | $\frac{9n}{(n^2+2)^2} \times 10^2$ |
|---|---|---|---|---|---|
| HCl .. | 1·36401 | 1·36575 | 1·37272 | 871 | 82·27 |
| LiCl .. | 1·36580 | 1·36752 | 1·37439 | 859 | 82·17 |
| NaCl .. | 1·36879 | 1·37051 | 1·37742 | 863 | 82·00 |
| KCl .. | 1·36811 | 1·36982 | 1·37666 | 855 | 82·04 |
| RbCl .. | 1·37194 | 1·37366 | 1·37953 | 859 | 81·82 |
| CsCl .. | 1·38108 | 1·38282 | 1·38980 | 872 | 81·31 |
| $NH_4Cl$ .. | 1·37018 | 1·37192 | 1·37887 | 869 | 81·92 |

TABLE IV

*The magneto-optic data for univalent bromide solutions*

| | M | $X_1$ | $X_2$ | $d$ | $V_{5461} \times 10^3$ | $[V_i]_M \times 10$ | 100$\gamma$ |
|---|---|---|---|---|---|---|---|
| HBr .. | 80·92 | 32·4 | 90·01 | 1·2238 | 23·56′ | 24·10′ | 79·5 |
| LiBr .. | 86·85 | 34·75 | 89·54 | 1·2428 | 23·65′ | 24·52′ | 81·1 |
| NaBr .. | 102·91 | 41·16 | 89·43 | 1·3059 | 24·56′ | 25·82′ | 84·3 |
| KBr .. | 119·09 | 47·60 | 84·72 | 1·3235 | 23·83′ | 26·81′ | 83·1 |
| $NH_4Br$ .. | 97·95 | 39·18 | 82·03 | 1·2121 | 23·98′ | 28·24′ | 84·4 |

TABLE V

*The optical data for univalent bromide solutions*
(4 *Normal*)

| | $n_{5893}$ | $n_{5461}$ | $n_{4358}$ | $\Delta n \times 10^5$ | $\frac{9n}{(n^2+2)^2} \times 10^2$ |
|---|---|---|---|---|---|
| HBr .. | 1·38192 | 1·38400 | 1·39232 | 1040 | 81·24 |
| LiBr .. | 1·38144 | 1·38349 | 1·39167 | 1023 | 81·27 |
| NaBr .. | 1·38532 | 1·38737 | 1·39555 | 1023 | 81·05 |
| KBr .. | 1·38330 | 1·38531 | 1·39337 | 1007 | 81·17 |
| $NH_4Br$ .. | 1·38681 | 1·38882 | 1·39689 | 1008 | 80·97 |

TABLE VI

*The magneto-optic data for univalent iodide solutions*
(4 *Normal*)

| | M | $X_1$ | $X_2$ | $d$ | $V_{5461} \times 10^3$ | $[V_i]_M \times 10$ | $100\gamma$ |
|---|---|---|---|---|---|---|---|
| HI .. | 127·92 | 51·16 | 85·76 | 1·3692 | 33·02′ | 49·40′ | 79·8 |
| LiI .. | 133·86 | 53·54 | 85·49 | 1·3903 | 33·62′ | 51·00′ | 82·9 |
| NaI .. | 149·91 | 59·96 | 83·26 | 1·4322 | 34·09′ | 53·04′ | 83·4 |
| KI .. | 166·02 | 66·41 | 80·78 | 1·4719 | 34·48′ | 54·96′ | 85·1 |
| $NH_4I$ .. | 144·96 | 57·98 | 78· 4 | 1·3692 | 34·70′ | 56·23′ | 84·7 |

TABLE VII

*The optical-data for univalent iodide solutions*
(4 *Normal*)

| | $n_{5893}$ | $n_{5461}$ | $n_{4358}$ | $\Delta n \times 10^5$ | $\frac{9n}{(n^2+2)^2} \times 10^2$ |
|---|---|---|---|---|---|
| HI .. | 1·39521 | 1·39811 | 1·40973 | 1452 | 80·45 |
| LiI .. | 1·41427 | 1·41711 | 1·42850 | 1423 | 79·54 |
| NaI .. | 1·41684 | 1·41971 | 1·43119 | 1435 | 79·24 |
| KI .. | 1·41520 | 1·41804 | 1·42943 | 1423 | 79·33 |
| $NH_4I$ .. | 1·41544 | 1·41831 | 1·42981 | 1437 | 79·31 |

## 4. THE MAGNETO-OPTIC ANOMALY OF THE IONS

From the data obtained in the previous section the magneto-optic anomaly of the ions as distinct from that of the solution can be calculated in the following way. The specific rotation of the ions can be calculated from one of the two mixture rules.

$$[V_s] = [V_i]\, x_1 + [V_\omega]\, x_2 \quad \text{— Verdet (1858)}$$

or

$$\frac{9n_s}{(n_s+2)^2}[V_s] = \frac{9n_i}{(n_i^2+2)^2}[V_i]\, x_1 + \frac{9n_\omega}{(n_\omega^2+2)^2}[V_\omega]\, x_2$$

de Mallemann (1926)

where [V] is the specific rotation, $n$ the refractive index and $x_1$ and $x_2$ the weight percentage of the salt and water. The subscripts $s$, $i$ and $w$ stand

for the solution, ions and water. The second formula has been derived from the first on the assumption that the Verdet rule is only true for gaseous mixtures and that in other cases, a correction for the Lorentz field has to be introduced. The correction factor was obtained from the accurate experimental results of de Mallemann and Gabiano (1933) who found that

$$[V]_{\text{vapour}} = \frac{9n_l}{(n_l^2+2)^2}\,[V]_{\text{liquid}}.$$

Although experiments have not yet decisively indicated the superiority of either of the mixture rules, the one due to de Mallemann is used in the following calculations as it has a greater theoretical justification. It is clear from the above that if the dispersion of the ions can be calculated from the dispersion data for the solutions the value of $\gamma$ for the ions can be evaluated.

The mixture rule for refraction is given by

$$\frac{n_s^2-1}{n_s^2+2}\times\frac{1}{d_s}=\frac{n_i^2-1}{n_i^2+2}\times\frac{1}{d_i}\,x_1+\frac{n_\omega^2-1}{n_\omega^2+2}\times\frac{1}{d_\omega}\,x_2$$

differentiating this equation we have

$$\frac{9n_s}{(n_s^2+2)^2}\frac{dn_s}{d\lambda}\times\frac{1}{d_s}=\frac{9n_i}{(n_i^2+2)^2}\frac{dn_i}{d\lambda}\times\frac{1}{d_i}\,x_1+\frac{9n_\omega}{(n_\omega^2+2)^2}\frac{dn_\omega}{d\lambda}\times\frac{1}{d_\omega}\,x_2$$

The dispersion of the ions can be directly calculated from this formula. If we put

$$\frac{n^2-1}{n^2+2}\times\frac{1}{d}=[R]\ \text{the refractivity.}$$

$$\frac{9n}{(n^2+2)^2}\times\frac{1}{d}\frac{dn}{d\lambda}=[D]\ \text{the dispersivity}$$

and

$$\frac{9n}{(n^2+2)^2}[V]=[\Omega]\ \text{the rotativity.}$$

Then the mixture rules can be written as

$$[R_s]=[R_i]\,x_1+[R_\omega]\,x_2 \quad \text{refraction}$$

$$[D_s]-[D_i]\,x_1+[D_\omega]\,x_2 \quad \text{dispersion}$$

$$[\Omega_s]=[\Omega_i]\,x_1+[\Omega_\omega]\,x_2 \quad \text{rotation (de Mallemann)}$$

$$[V_s]=[V_i]\,x_1+[V_\omega]\,x_2 \quad \text{rotation (Verdet)}$$

Since $V=\gamma\, e/2mc^2\ (\lambda\, dn/d\lambda)$

$$\gamma_{\text{ion}}=\frac{[\Omega_i]}{\dfrac{e}{2mc^2}\,\lambda\,[D_i]}$$

The formulæ given above make the following assumptions (*a*) the Lorentz-Lorenz formula for refraction is true in ionic assemblies and (*b*) the optical and magneto-optical properties of water do not change due to the presence of the ions in solution. It is also quite obvious that the value of $\gamma$ obtained by this method gives only the anomaly of the hydrated or solvated ion.

Table VIII gives value of $\gamma_{ion}$ for the 17 halides calculated from the data given in Tables II to VII. The table also gives the value of the Molecular Dispersivity $[D_i]_M = M\,[D_i]$ the molecular rotativity $[\Omega_i]_M$ and the molecular rotation $[V_i]_M$ of the alkali halides ion in solution. The errors in the values of $[D_i]_M$, $[\Omega_i]_M$, $[V_i]_M$ and $\gamma_{ion}$ would be of the order of 3 to 4 per cent.

TABLE VIII

| | $[D_i]_M$ | $[V_i]_M$ | $[\Omega_i]_M$ | $100\gamma$(ions) |
|---|---|---|---|---|
| HCl .. | 11·57 | 12·61 | 9·73 | 84 |
| LiCl .. | 10·76 | 13·10 | 10·01 | 93 |
| NaCl .. | 11·33 | 14·50 | 11·14 | 98 |
| KCl .. | 12·46 | 15·45 | 12·00 | 96 |
| RbCl .. | 13·38 | 16·70 | 12·89 | 96 |
| CSCl .. | 15·10 | 19·82 | 15·24 | 101 |
| $NH_4Cl$ .. | 14·55 | 16·72 | 12·94 | 89 |
| HBr .. | 21·64 | 24·10 | 18·59 | 86 |
| LiBr .. | 20·89 | 24·52 | 18·95 | 91 |
| NaBr .. | 20·75 | 25·82 | 20·67 | 99 |
| KBr .. | 21·88 | 26·81 | 20·80 | 95 |
| $NH_4Br$ .. | 22·22 | 28·24 | 19·82 | 86 |
| HI .. | 50·7 | 49·40 | 38·5 | 76 |
| LiI .. | 43·7 | 51·00 | 39·0 | 90 |
| NaI .. | 45·0 | 53·04 | 40·5 | 91 |
| KI .. | 45·8 | 54·96 | 42·0 | 91 |
| $NH_4I$ .. | 47·2 | 56·23 | 43·2 | 91 |

## 5. DISCUSSION OF RESULTS

From the scrutiny of the tables, one notices that while the contribution of the anion to the magnetic rotation is considerable, that due to the cation is comparatively small. Further the variation in rotation produced by a change in the acid radical is much more pronounced than that produced by a change in the metallic radical. Table IX gives the differences of the values of $[V_i]_M$ for the compounds. From these the molecular magnetic rotation of individual ions may be computed if the value for one of the ions is arbitrarily fixed. As an approximation, it may be assumed that the rotation due to the hydrogen ion is zero. On this basis the average ionic rotations have been computed and given in Table X. Since the values for the cations are small they are less accurate than those for the anions.

If the ionic rotations are plotted against the atomic number, curves very similar to those obtained by Fajans and his collaborators (1924) for ionic volumes and ionic refractivities are obtained. One can see that the additivity rule is only approximately valid. This is probably because the solutions are too concentrated. But unfortunately in the case of dilute solutions the rule cannot be tested as large errors enter in the measurement of the dispersion and Faraday rotation.

TABLE IX

*Molecular rotation in mins.* × 10

| | H | Li | Na | K | $NH_4$ |
|---|---|---|---|---|---|
| Cl—F .. | .. | .. | 12·30 | 12·20 | 12·00 |
| Br—Cl .. | 11·49 | 11·42 | 11·27 | 11·36 | 11·52 |
| I—Cl .. | 36·79 | 37·90 | 38·54 | 39·51 | 39·46 |

| | Cl | Br | I |
|---|---|---|---|
| Li—H .. | 0·59 | 0·42 | 1·60 |
| Na—Li .. | 1·40 | 1·30 | 2·04 |
| K—Li .. | 2·35 | 2·29 | 3·96 |
| $NH_4$—Li .. | 3·62 | 3·72 | 5·23 |

TABLE X

*Ionic rotations in mins.* × 10

| H | Li | Na | K | Rb | CS | $NH_4$ | Cl | Br | I |
|---|---|---|---|---|---|---|---|---|---|
| e | 0·60 | 1·72 | 2·70 | 4·09 | 7·21 | 4·15 | 12·41 | 24·10 | 49·40 |

Table XI give the $\gamma$ values for the different halide solutions. The value of $\gamma$ for water is 0·76. One notices that the presence of the halides of alkali metals in water increases its $\gamma$ value. This obviously means that the $\gamma$ value of the ions is higher than that of water, a fact which finds proof from the figures in Table VIII. The experiments of the author on crystals (*loc. cit.*) indicate that the presence of covalent linkages tend to reduce the value of $\gamma$. If this were true the lower values of $\gamma$ of HCl, HBr and HI than those for the corresponding halides of the alkali metals may either be due to the acids

not being completely dissociated or due to the formation of other types of groups by the free hydrogen ions. The values of the anomaly for the pure acids HCl and HBr are respectively 62% and 38%. The low values are most probably due to the covalent linkages that are known to be present in these acids in the pure state. In solutions, however, the values of $\gamma$ are higher than those for the pure acids because of the ionisation.

TABLE XI

*The magneto-optic anomaly of 4 normal solution*

$100\gamma$

| | H | Li | Na | K | $NH_4$ |
|---|---|---|---|---|---|
| Cl .. | 77·8 | 79·6 | 81·4 | 81·1 | 79·6 |
| Br .. | 79·5 | 81·1 | 84·3 | 83·1 | 83·4 |
| I .. | 79·8 | 82·9 | 83·4 | 85·1 | 84·7 |

As already pointed out Rosenfeld has shown that for gases having the inert gas configuration the value of $\gamma$ is unity. The author has calculated the values of $\gamma$ for argon and neon from the optical and magneto-optic data given in Landolt and Bornstein Tables. The values of the Verdet constant and the value of the anomaly for these gases are given in Table XII.

TABLE XII

*The magneto-optic anomaly in rare gases*

| Gas | $V_{5461} \times \frac{10^{-6} \text{ min.}}{\text{per cm. per oersted}}$ | $100\gamma$ |
|---|---|---|
| Neon .. | 1·1 | 116·5 |
| Argon .. | 9·2 | 100·6 |

One notices that the values of $\gamma$ for these gases are 1·16 and 1·00. Neon has an exceedingly small Verdet constant of $1{\cdot}1 \times 10^{-6}$ minutes per cm. per oersted; only a sixth of the value found in hydrogen gas. Since no other substance has been found to have a $\gamma$ value of more than 1, it is quite probable that this high value of $\gamma$ in neon is due to experimental errors.

Since free ions of the alkali metals and the halogens have the inert gas configuration they too should obey the Becquerel formula, *i.e.*, $\gamma = 1$. Table VIII shows that $\gamma$ value of the ions in solution varies from 0·90 to 1·00. It must be remembered that in the calculation of the anomaly for the ions

many assumptions have been made, for instance the validity of the Lorentz-Lorenz formula for refraction in ionic assemblies. Further the values of $\gamma$ found are those for solvated or hydrated ions and the energy of solvation as found from absorption spectra data (Gurney, 1936) is quite considerable. Nevertheless these experiments and calculations show *that in inert gases and in ions having the inert gas configuration the Faraday effect very nearly obeys the unmodified Becquerel formula* (*i.e.*, $\gamma = 1{\cdot}00$).

Fajans and Joos (1924) have found that the molecular refractivity of ions in solution is much larger than the value for the same ions in the crystalline state. This difference in the refractivity they attribute to the distortion of the electron atmospheres by the crystalline fields. Table XIII gives a collection of the data of molecular refractivity dispersivity, magnetic rotativity magnetic rotation and the magneto-optic anomaly for ions in solution and the crystalline state for the four substances NaCl, KCl, KBr and KI.

TABLE XIII

*Refractive and magneto-optic constants of crystals and their solutions*

| Substance | $[R_i]_M$ | | $[D_i]_M$ | | $[\Omega_i]_M$ | | $[V_i]_M$ | | 100γ ion | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Cry. | Soln. | Cry. | Soln. | Cry. | Soln. | Cry. | Soln. | Cry. | Soln. |
| NaCl .. | 8·57 | 9·469 | 8·18 | 11·33 | 8·09 | 11·14 | 11·08 | 14·50 | 90 | 98 |
| KCl .. | 10·90 | 11·43 | 10·22 | 12·46 | 9·23 | 12·00 | 12·29 | 15·45 | 82 | 96 |
| KBr .. | 14·05 | 15·05 | 18·38 | 21·88 | 15·41 | 20·80 | 21·63 | 26·81 | 79 | 95 |
| KI .. | 19·92 | 21·76 | 35·90 | 45·80 | 28·74 | 42·00 | 44·01 | 54·96 | 79 | 91 |

It is clear from the table that in every case the value of the constant for the ions in solution is much greater than that for the ions in the crystalline state. One notices also that these differences are largest in the case of the magnetic rotation and rotativity. These figures seem to indicate that Faraday effect can be used as a sensitive tool for the determination of any distortions in the electron atmospheres in atoms or ions.

In conclusion, the author wishes to thank Prof. R. S. Krishnan for the kind interest he took in these investigations.

## SUMMARY

The Verdet constant and dispersions of 4-normal solutions of seventeen univalent halides have been measured. From these, the values of the magneto-optic anomaly have been estimated. The magneto-optic anomaly of the

free ions of the alkali halides as distinct from that of the solution have been evaluated. It is found that the value of the anomaly of the free ions having the inert gas configuration is very near the theoretical value of 1. The ionic dispersivity and rotativity of the individual ions have been estimated. It is found that the additivity rule is approximately valid. The pure acids, HCl, HBr and HI, have values of the anomaly much lower than those for their solutions. This has been attributed to the presence of covalent linkages in the acids in the pure state. The anomaly for the rare gases neon and argon are very nearly unity. It is found that the values of molecular refractivity, dispersion, rotativity, rotation and the magneto-optic anomaly of the ions in solution are higher than those for the ions in the crystalline state.

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# FORMATION OF COMPLEX COMPOUNDS BETWEEN LEAD NITRATE AND POTASSIUM NITRATE

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## 1. Introduction

The proposition that a complex compound is formed between lead nitrate and potassium nitrate when they are in aqueous solution was put forward by Lewis (1908, 1923) in order to account for the observed increase in the solubility of lead nitrate in water when potassium nitrate was added. This was first noticed by Leblanc and Noyes (1890). Lewis and Kanitz later confirmed this observation. Lewis suggested that lead nitrate and potassium nitrate combined to form a double salt which in the presence of water ionized forming a complex ion.

$$KNO_3 + Pb(NO_3)_2 \rightarrow (KPbNO_3)^{++} + 2NO_3^{-}$$

But the reaction suggested above has been shown by Glasstone to be inconsistent with the electronic theory of valency. Various alternative forms have been suggested. It is to be remembered at the same time that no complex formation has been observed in the solid state. Recently, Nayar and Pande (1948, 1949) carried out a systematic investigation of some of the properties of mixtures of aqueous solutions of potassium nitrate and lead nitrate. From the measurements of viscosity, surface tension, electromotive force, transport number, conductivity and magnetic susceptibility of mixtures of aqueous solutions of the above nitrates, they have concluded that three double salts are formed and these undergo ionization due to the presence of water. These double salts are

$KNO_3Pb(NO_3)_2 \cdot H_2O$ $2KNO_3Pb(NO_3)_2 \cdot H_2O$ and $4KNO_3Pb(NO_3)_2 \cdot H_2O$.

In view of the importance of the subject, it was considered desirable to investigate the Faraday effect and the resulting magneto-optic anomaly of mixtures of molar solutions of these nitrates, a property which is indicative of the nature of the forces inside the medium. If complex ions are formed for specified concentrations of the mixture, the curves representing the variation of the Faraday rotation and the magneto-optic anomaly with concentration may be expected to exhibit discontinuities in their course. As we shall see, however, the results of the present investigation are in

accordance with the above expectations. Incidentally, the author has also investigated the other optical properties of the mixtures of potassium and lead nitrates, namely refractive index, refractivity and dispersion.

## 2. Experimental Details

The experiment consisted in preparing molar solutions of potassium nitrate and lead nitrate and a number of their mixtures with different relative concentrations and measuring the Faraday rotation of the plane of polarization, the density and the refractive indices for different wavelengths for each of these mixtures. The molar solutions were carefully prepared and were preserved in stoppered bottles. Pure Kahlbaum chemicals were used. Thirty-one different mixtures were prepared. The volume of each mixture was twelve c.c. and the compositions of all the mixtures are given in the table presented below. The solutions of the pure salts were filled in two burrettes and the required volume of each was let into a small flask provided with a stopper. When the volume of one of the components happened to be less than one c.c. a pipette graduated in 0·01 c.c. was used instead of a burette. Thus thirty-one samples of the mixture with different concentrations were prepared and preserved in stoppered flasks.

The Faraday rotation of the plane of polarization in a magnetic field of known strength was measured relative to the rotation in water, the lengths of the liquid column and water column being the same. The measurement was repeated for all the mixtures. Finally the rotation of the plane of polarization in water was measured relative to the rotation in an identical column of air. Thus the absolute rotation of the plane of polarization could be obtained. The electromagnet which provided the necessary field was of the Rutherford type. The pole pieces had longitudinal holes about 0·6 cm. in diameter. With an exciting current of 6 Amps. a field of the order of 16,000 gauss could be produced, when the gap between the pole pieces was one cm. and the field is constant to within 2 to 3% across the hole. For the present investigation, however, the field utilized was only about 8,000 gauss. The exciting current was 6 Amps. and the gap between the pole pieces was about three cm. Although no water cooling was provided, the magnet could be used continuously for an hour without the coils becoming appreciably hot. Hence it was found necessary to work intermittently with an interval of an hour during which time the coils would get cooled. The liquid under investigation was kept in a glass cell whose thickness could be measured very accurately. Water was kept in another cell whose thickness was identical with the thickness of the first cell. The two were mounted on a sliding arrangement so that one or the other of the

two cells could be slid across the holes in the pole pieces. The whole system was rigidly fixed by means of wax so that the position of the sliding arrangements as a whole did not move when the sliding portion was moved back and forth.

The source of light used was a point source mercury lamp. By inserting a suitable filter, mercury green radiation was isolated and was condensed on the polarizer by means of a water-cooled condenser. The rotation was measured by means of a polarimeter which was fitted with a circular scale which could give readings up to 0·01°. The polarimeter was provided with a double field polarizer, in which the half shadow angle could be varied from 0° to 20°, but it was found convenient to work with a half shadow angle of 5°. When the matching was repeated for the same mixture, the readings differed by 0·01° or 0·02° and often the same readings were obtained. For each solution matching was repeated a dozen times and the mean value of the several readings obtained was taken. By this method the rotations relative to water in all the thirty-one samples were determined. Lastly, one of the cells was thoroughly washed and dried. This was mounted along with the other containing water. Thus the rotation in water relative to that in air could be measured. Now assuming the Verdet's constant of water for 5461 Å to be 0·01547 mins. of an arc per cm. per gauss the Verdet's constant for each of the mixtures was found out. Good agreement was noticed when the experiment was repeated for a different set of mixtures.

The refractive index of each of the mixtures was determined by means of a Pulfrich Refractometer, which could give the value of refractive index to five places of decimals. The refractive indices for wave lengths 4358 Å, 5461 Å, 5770 Å, 5790 Å and 5893 Å were determined. From these values, the dispersion could be easily calculated. Thus, knowing the value of Verdet's constant in the case of each mixture and the dispersion in each mixture, the value of the magneto-optic anomaly could be evaluated from the well-known equation of Becquerel (1877) which as modified by Darwin and Watson (1927) is given as

$$V = \gamma \frac{e}{2m^2c} \cdot \lambda \cdot \frac{dn}{d\lambda},$$

$\gamma$ being the magneto-optic anomaly, $e$ and $m$, being the charge and mass of the electron and $c$ the velocity of light, V being the Verdet's constant of the substance for wavelength $\lambda$.

The specific gravity of each of these mixtures was determined by means of a specific gravity bottle with the usual precautions to obtain accurate

values. Since we know the values of refractive index and specific gravity we can calculate the refractivity from the formula

$$[R] = \frac{n^2 - 1}{n^2 + 2} \cdot \frac{1}{d}.$$

### 3. Results

Table I gives the composition, the density, the value of $n_{5461}$ and $n_{4358}$ and the values of $[R]_{5461}$ and $[R]_{4358}$ of each solution at a temperature of $24 \pm 1°$ C.

Table I

| Solution No. | Vol. of (M)·$KNO_3$ solution in 12 c.c. of Mix. | Sp Gr. | $n_{5461}$ | $n_{4358}$ | $[R]_{5461}$ | $[R]_{4358}$ |
|---|---|---|---|---|---|---|
| 1 | 0 | 1·265 | 1·36945 | 1·37646 | 0·1785 | 0·1829 |
| 2 | 0·5 | 1·260 | 1·37064 | 1·37779 | 0·1797 | 0·1829 |
| 3 | 1·0 | 1·253 | 1·36873 | 1·37596 | 0·1799 | 0·1831 |
| 4 | 1·5 | 1·246 | 1·36682 | 1·37421 | 0·1801 | 0·1834 |
| 5 | 2·0 | 1·237 | 1·36385 | 1·37105 | 0·1801 | 0·1844 |
| 6 | 2·5 | 1·229 | 1·36323 | 1·37049 | 0·1809 | 0·1845 |
| 7 | 3·0 | 1·219 | 1·36245 | 1·36968 | 0·1820 | 0·1854 |
| 8 | 3·5 | 1·211 | 1·36162 | 1·36886 | 0·1828 | 0·1854 |
| 9 | 4·0 | 1·203 | 1·36156 | 1·36889 | 0·1839 | 0·1863 |
| 10 | 4·5 | 1·194 | 1·35870 | 1·36580 | 0·1841 | 0·1875 |
| 11 | 5·0 | 1·186 | 1·35815 | 1·36503 | 0·1851 | 0·1884 |
| 12 | 5·5 | 1·178 | 1·35670 | 1·36362 | 0·1857 | 0·1889 |
| 13 | 5·7 | 1·173 | 1·35670 | 1·36360 | 0·1865 | 0·1898 |
| 14 | 6·0 | 1·170 | 1·35611 | 1·36254 | 0·1867 | 0·1898 |
| 15 | 6·3 | 1·164 | 1·35611 | 1·36254 | 0·1877 | 0·1908 |
| 16 | 6·5 | 1·163 | 1·35399 | 1·36077 | 0·1868 | 0·1902 |
| 17 | 7·0 | 1·153 | 1·35340 | 1·36023 | 0·1880 | 0·1950 |
| 18 | 7·5 | 1·146 | 1·35382 | 1·36069 | 0·1893 | 0·1928 |
| 19 | 7·7 | 1·144 | 1·35252 | 1·35986 | 0·1892 | 0·1930 |
| 20 | 8·0 | 1·138 | 1·35163 | 1·35839 | 0·1898 | 0·1931 |
| 21 | 8·3 | 1·135 | 1·35171 | 1·35839 | 0·1904 | 0·1936 |
| 22 | 8·5 | 1·129 | 1·35166 | 1·35834 | 0·1914 | 0·1946 |
| 23 | 9·0 | 1·121 | 1·35079 | 1·35734 | 0·1924 | 0·1948 |
| 24 | 9·3 | 1·114 | 1·35938 | 1·35572 | 0·1926 | 0·1958 |
| 25 | 9·5 | 1·113 | 1·34928 | 1·35572 | 0·1927 | 0·1961 |
| 26 | 9·9 | 1·107 | 1·34798 | 1·35531 | 0·1932 | 0·1970 |
| 27 | 10·0 | 1·104 | 1·34798 | 1·35514 | 0·1938 | 0·1974 |
| 28 | 10·5 | 1·094 | 1·34726 | 1·35342 | 0·1950 | 0·1982 |
| 29 | 11·0 | 1·084 | 1·34592 | 1·35226 | 0·1962 | 0·1994 |
| 30 | 11·5 | 1·075 | 1·34511 | 1·35157 | 0·1975 | 0·2009 |
| 31 | 12·0 | 1·069 | 1·34454 | 1·35089 | 0·1985 | 0·2015 |

Table II gives the rotation, Verdet's constant, the value of $\Delta n$ which is equal to $(n_{4358} - n_{5461})$ and the value of $\gamma$ expressed as a percentage for each mixture at a temperature of $24 \pm 1°$ C.

In order to understand how the optical properties vary as the composition of the mixtures varies from 100% lead nitrate solution to 100% potassium nitrate solution, it is necessary to study the accompanying graph

TABLE II. *Length of the column* 1·820 *cm.* $H = 7900$ *gauss*

| Solution No. | $\theta°$ | V | $\Delta n \times 10^3$ | $100\gamma$ |
|---|---|---|---|---|
| 1 | 4·21 | 0·01761 | 7·01 | 72·4 |
| 2 | 4·21 | 0·01761 | 7·15 | 72·0 |
| 3 | 4·20 | 0·01756 | 7·23 | 71·0 |
| 4 | 4·20 | 0·01756 | 7·39 | 70·5 |
| 5 | 4·16 | 0·01739 | 7·20 | 71·7 |
| 6 | 4·14 | 0·01731 | 7·26 | 70·7 |
| 7 | 4·12 | 0·01723 | 7·23 | 70·6 |
| 8 | 4·10 | 0·01716 | 7·25 | 70·1 |
| 9 | 4·08 | 0·01706 | 7·20 | 70·0 |
| 10 | 4·04 | 0·01688 | 7·10 | 70·2 |
| 11 | 4·02 | 0·01680 | 6·88 | 71·3 |
| 12 | 3·98 | 0·01663 | 6·92 | 71·2 |
| 13 | 3·96 | 0·01655 | 6·90 | 71·0 |
| 14 | 3·95 | 0·01652 | 6·43 | 76·1 |
| 15 | 3·96 | 0·01655 | 6·43 | 76·4 |
| 16 | 3·98 | 0·01643 | 16·78 | 71·7 |
| 17 | 3·93 | 0·01643 | 6·83 | 71·7 |
| 18 | 3·89 | 0·01627 | 6·87 | 69·3 |
| 19 | 3·81 | 0·01592 | 7·34 | 64·3 |
| 20 | 3·77 | 0·01576 | 6·77 | 69·1 |
| 21 | 3·77 | 0·01575 | 6·72 | 73·1 |
| 22 | 3·84 | 0·01505 | 6·68 | 73·5 |
| 23 | 3·82 | 0·01597 | 6·55 | 73·2 |
| 24 | 3·79 | 0·01584 | 6·36 | 73·8 |
| 25 | 3·72 | 0·01556 | 6·44 | 71·6 |
| 26 | 3·74 | 0·01564 | 7·33 | 63·2 |
| 27 | 3·77 | 0·01576 | 7·16 | 65·2 |
| 28 | 3·73 | 0·01559 | 6·16 | 75·0 |
| 29 | 3·70 | 0·01547 | 6·24 | 73·4 |
| 30 | 3·64 | 0·01522 | 6·46 | 70·2 |
| 31 | 3·65 | 0·01525 | 6·35 | 71·0 |

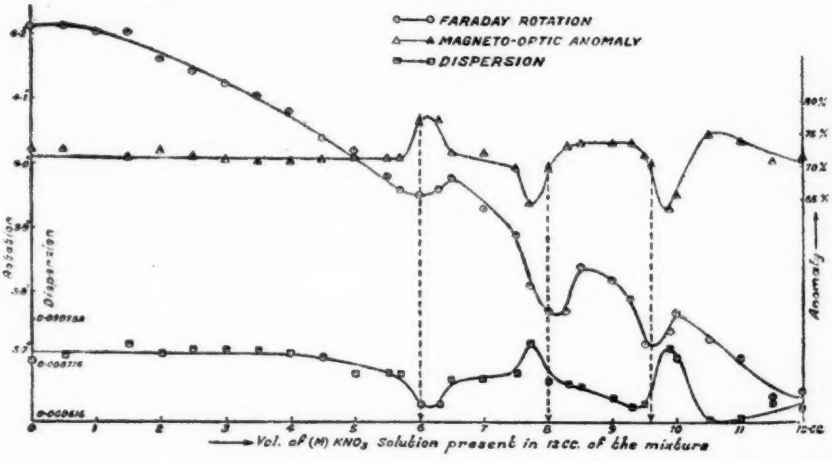


FIG. 1

which exhibits the variation of the rotation, $\Delta n$ and $\gamma$ as the composition gradually changes. The abscissa denotes the volume of molar solution of potassium nitrate in the mixture whose volume is twelve c.c. What is very striking is the presence of peaks and troughs at approximately the same points in all three curves. These points are close to the points which correspond to the relative concentrations of lead nitrate to potassium nitrate in the ratio of 1 : 1, 1 : 2, 1 : 4. The slight departure may be ascribed to the possible errors in the preparation of the mixtures. At these points there is a remarkable departure from what may be expected of an ordinary simple mixture. These may be attributed to the formation of complex ions. According to Lewis, complex ions are present irrespective of the relative concentration, since the solubility of lead nitrate at once increases as soon as potassium nitrate is added. Probably the complex ions are predominant at the three critical concentrations. The refractive index curve and the refractivity curve which are not reproduced here also exhibit some interesting features. The refractivity curve consists of four lines which are almost parallel to one another with three plateaus in between. The mid-points of the three flat portions of the curve correspond roughly to the critical concentrations. The refractive index curve also exhibit some special features at the three critical points. Just before a critical point the curve becomes almost flat and then there is a steep fall followed by a flattening and away from the critical point the curve exhibits a uniform variation. Besides these critical points mentioned above, two more points are noticed at which there is a sudden change in the curvature, these being, however, less conspicuous. These correspond roughly to the concentrations of lead nitrate to potassium nitrate in the ratio of 5 : 1 and 2 : 1 rspectively. But for these additional features, there is good agreement between the results obtained by the present writer and those obtained by Nayar and Pande, working essentially in diverse fields. Besides confirming the suggestions regarding the complex ion formation in aqueous solution of lead nitrate and potassium nitrate, the present investigation has revealed the utility of Faraday effect measurements for such studies.

## 4. Acknowledgements

I have got great pleasure in expressing my gratitude to Prof. R. S. Krishnan for suggesting this line of investigation and his keen interest in the work. I thank Mr. S. Ramaseshan for helpful discussions.

## Summary

A systematic investigation of the optical properties, namely, refractive index, refractivity dispersion and rotation of the plane of polarization in a

magnetic field of mixtures of the molar solutions of lead nitrate and potassium nitrate has been carried out. The properties show a remarkable departure from what may be expected of an ordinary mixture at relative concentrations of lead nitrate and potassium nitrate in the ratio of 1 : 1, 1 : 2 and 1 : 4. The refractive index curve showed some additional features at relative concentrations of lead nitrate and potassium nitrate in the ratio 5 : 1 and 2 : 1, these being, however, less conspicuous than the other three mentioned above. These departures at the three critical concentrations may be ascribed to the presence of complex ions of $KNO_3\ Pb(NO_3)_2 \cdot H_2O$, $2KNO_3\ Pb(NO_3)_2 \cdot H_2O$ $4KNO_3\ Pb(NO_3)_2 \cdot H_2O$ respectively as suggested by Nayar and Pande.

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# RAMAN SPECTRA OF CRYSTALLINE TARTRATES

## Part III. Tartaric Acid

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(Communicated by Prof. R. S. Krishnan, F.A.SC.)

### 1. Introduction

In Parts I and II of this series, the author (Padmanabhan, 1948, 1950) described the results obtained from studies on the Raman spectra of crystalline sodium tartrate, potassium tartrate, ammonium tartrate and Rochelle salt, using $\lambda 2536$ mercury resonance radiation as exciter. This paper gives an account of a similar investigation carried out with tartaric acid in the form of a single crystal. Its Raman spectrum was photographed simultaneously by Canals and Peyrot (1938) and by Gupta (1938). In both these investigations the visible radiation of the mercury arc was employed for exciting the Raman spectrum. Canals and Peyrot, who used the powder technique, reported the existence of 13 Raman lines with frequency shifts 737, 891, 993, 1094, 1260, 1309, 1364, 1691, 1745, 2931, 2964, 3331 and 3422 cm.$^{-1}$ Gupta, on the other hand, employed a single crystal, and identified eleven Raman lines in the spectrum with frequency shifts 37, 80, 103, 125, 731, 848, 895, 1140, 1745, 2934 and 2967 cm.$^{-1}$ It is indeed surprising to note that these authors had in common observed only five frequency shifts. A detailed investigation of the Raman effect in crystalline tartaric acid is therefore called for.

### 2. Experimental Details and Results

Crystals of tartaric acid were grown by the method of slow evaporation from aqueous solutions of the pure substance. The specimens used for photographing the Raman spectrum had the size $2 \times 1 \times 1$ cm. The direction of illumination was roughly normal to the face (100) and the direction of observation was nearly normal to the (001) face. An enlarged photograph of its Raman spectrum taken with a Hilger medium quartz spectrograph with a slit-width of 0·035 mm. and an exposure of the order of a day is reproduced in Fig. 1. The positions and frequency shifts are marked in the figure. The frequencies are listed in Table I, along with the 19 frequency shifts already observed by earlier workers. The figures in brackets represent visual estimates of the relative intensities of the lines. The frequency shifts

observed by Edsall (1937) in the spectrum of tartaric acid solution are also included in the same table. The Raman spectrum of tartaric acid exhibits thirty-one lines which include the line at 1745 cm.$^{-1}$ reported by Canals

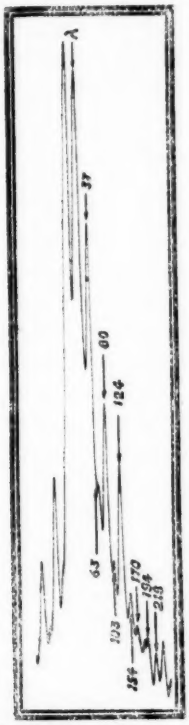


FIG. 2. Microphotometer record of the lattice spectrum of tartaric acid

and Peyrot and by Gupta. This line could not be identified in the spectrogram taken by the author with $\lambda$ 2536 excitation as it would have fallen on the mercury triplet $\sim\lambda$ 2652. The author has not only confirmed the existence of all the 13 frequency shifts observed by Canals and Peyrot and the 11 by Gupta, but also recorded the following twelve new frequency shifts 63, 154, 170, 194, 218, 293, 317, 538, 787, 1126, 1265, and 1451 cm.$^{-1}$

In the low frequency shift region, the spectrum exhibits nine lines which are exceptionally sharp. Of these three at 37, 80 and 103 cm.$^{-1}$ are very prominent, the remaining six lines although feeble in intensity are clearly discernible in the spectrogram. They are more easily seen in the microphotometer record reproduced in Fig. 2. The line with the smallest frequency shift, namely 37 cm.$^{-1}$, is the most intense one.

The first six lines 37, 63, 80, 103, 124 and 154 cm.$^{-1}$ exhibit a periodic variation in intensity, the absolute intensity of all the lines diminishing gradually with increasing frequency shift. Further there is nearly the same frequency difference (of the order of 45 cm.$^{-1}$) between the consecutive odd lattice lines, 37, 80, 124, 170 and 218 cm.$^{-1}$

TABLE I. *Raman spectrum of tartaric acid crystal*

| Tartaric acid crystal | | Tartaric acid solution | Tartaric acid crystal | | Tartaric acid solution |
|---|---|---|---|---|---|
| Author | Previous workers | | Author | Previous workers | |
| 37 (20) | 37 | | | | 937 |
| 53 (6) | | | 991 (2) | | 1009 |
| 80 (15) | 80 | | 1093 (1) | 1094 | |
| 103 (5) | 103 | | 1126 (8) | | 1119 |
| 124 (10) | 125 | | 1140 (6) | 1140 | |
| 154 (3) | | | 1250 (6) | 1260 | 1232 |
| 170 (1) | | | 1265 (6) | | |
| 194 (1) | | | 1307 (3) | 1309 | |
| 218 (1) | | | 1359 (4) | 1364 | |
| | | 233 | 1451 (2) | | 1432 |
| 293 (1) | | | | | 1632 |
| 317 (1) | | 376 | 1698 (3) | 1698 | |
| 538 (3)$b$ | | 532 | 1745 | 1745 | 1732 |
| | | 669 | 2934 (10) | 2934 | 2936 |
| 731 (12) | 731 | 739 | 2967 (15) | 2967 | |
| 787 (3) | | 817 | 3322 (10) | 3331 | |
| 868 (6) | 848 | 870 | 3407 (8) | 3422 | |
| 891 (6) | 891 | | | | |

Fig. 3 represents the Raman spectra of tartaric acid, ammonium tartrate, potassium tartrate, sodium tartrate and Rochelle salt taken with the medium quartz spectrograph and enlarged to the same extent. It is evident from the figure that the spectrum of tartaric acid exhibits the minimum number of Raman lines. Regarding the sharpness of the lines, the tartrate frequencies of ammonium tartrate are sharper than those of tartaric acid, while the converse is true for the lattice lines.

## 3. DISCUSSION

The crystal structure of tartaric acid has been analysed using the X-ray method by Astbury (1922). The structure belongs to the monoclinic class. X-ray investigations reveal that there are two molecules in a unit cell and that the crystal belongs to space group $C_2^2$. The two molecules in the fundamental cell are held together end to end by forces between the hydrogen atoms of adjacent hydroxyl groups. The plane in which these molecular junctions lie is the plane 100, the perfect cleavage plane of the crystal.

*Lattice frequencies.*—On the basis of the structure given above, it is possible to understand the appearance of 9 lattice lines in the spectrum of crystalline tartaric acid, as indicated below. The elements of symmetry for the unit cell containing two molecules are (1) identity E and (2) one two-fold screw axis $C_2$. The full character table for this structure is given in Table II where T and R give the number of translatory and rotatory modes inside the

TABLE II

| $C_2^2$ | E | $C_2$ | $n_i$ | External $i$ | | Raman | Infra-red |
|---|---|---|---|---|---|---|---|
| | | | | T | R | | |
| A .. | 1 | 1 | 48 | 2 | 3 | active | active |
| B .. | 1 | −1 | 48 | 1 | 3 | active | active |
| $U_R$ .. | 32 | 0 | | | | | |
| $U_{R(s)}$ .. | 2 | 0 | | | | | |
| $U_{R(s-v)}$ .. | 2 | 0 | | | | | |
| $h_\rho x_\rho'$ (T) .. | 3 | 1 | | | | | |
| $h_\rho x_\rho'$ (R) .. | 6 | 0 | | | | | |

lattice. There are on the whole nine of these modes, which are both Raman and infra-red active, five of which come under class A and four under class B. For a proper assignment of the observed lattice lines, it is necessary to study the state of polarisation of the lattice lines. The specimen of tartaric acid used in the present investigation was rather small and did not have all its faces well developed. Hence the effect of crystal orientation on the intensities and state of polarisation of the lattice lines was not studied. It is proposed to take up this investigation in the near future.

*Internal frequencies.*—The twenty-two Raman lines with frequency shifts lying in the region 250 to 3500 cm.$^{-1}$ arise from the internal oscillations of the tartaric acid molecule. It is natural to expect a close correspondence between these frequency shifts and those observed in the spectrum of the tartaric acid solution (see Table I). The following peculiarities may be mentioned.

The line at 2936 cm.$^{-1}$ observed in the spectrum of the solution is split into two with frequency shifts 2934 and 2967 cm.$^{-1}$ in the case of crystal. The lines at 1119 and 1232 cm.$^{-1}$ in the spectrum of tartaric acid solution, which are due to C-OH group oscillation, appear as doublets with frequency shifts 1126 and 1140, 1250 and 1265 cm.$^{-1}$ in the spectrum of the tartaric

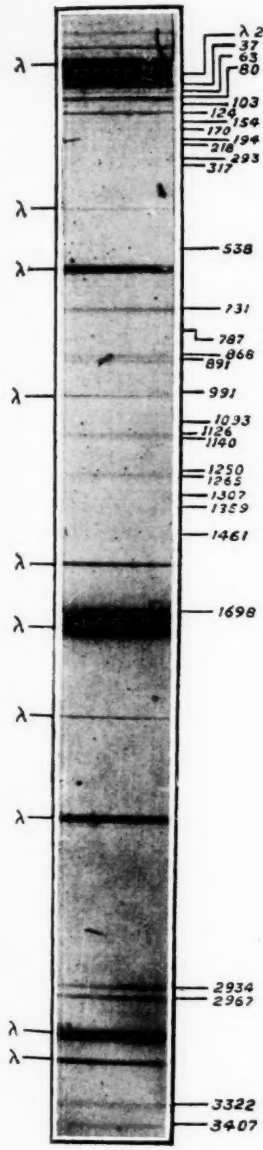


FIG. 1. Raman spectrum of crystalline tartaric acid taken with a Hilger medium quartz spectrograph.

FIG. 3. Raman spectra of crystalline : (*a*) tartaric acid, (*b*) ammonium tartrate, (*c*) potassium tartrate, (*d*) sodium tartrate, (*e*) Rochelle salt.

acid crystal. The two lines at 3322 and 3407 cm.$^{-1}$ which are roughly equal in intensity are due to O-H oscillations. The remaining lines (arising from oscillations due to C—C, C—OH, and C=O groups) show fairly one to one correspondence in the spectra of the crystal and of the solution.

In conclusion, the author wishes to record his deep sense of gratitude to Prof. R. S. Krishnan for his guidance and encouragement.

## 4. Summary

The Raman effect in a single crystal of tartaric acid has been investigated using the $\lambda$ 2536 mercury resonance radiation as exciter. The spectrum exhibited twelve new lines in addition to the nineteen lines observed previously. The 31 frequency shifts recorded here are made up of 9 lattice lines and 22 lines due to internal oscillations.

The most striking feature of the Raman spectrum of crystalline tartaric acid is the fact that the lattice lines are sharper than the lines arising from internal oscillations. They are more or less equally spaced and the alternate lines exhibit a remarkable gradation in intensity.

A close correspondence is noticed between the tartrate frequencies of tartaric acid crystal and those of tartaric acid solution.

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# THE MAGNETO-OPTIC ANOMALY OF ELECTROLYTES IN AQUEOUS SOLUTION—II

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## 1. INTRODUCTION

IN a preliminary study by the author on the magneto-optic anomaly in electrolytic solutions (Ramaseshan, 1948) it was noticed that solutions of the alkali halides had values of the anomaly greater than that for water. On the other hand the presence of sodium chlorate and the alums in water always decreased its $\gamma$ value. This difference in behaviour between the simple alkali halide ion and the other more complicated ones induced the author to undertake a systematic measurement of the magneto-optic and optical constants of a large number of ionic solutions. In a previous paper (1950) the results obtained with seventeen univalent halide solutions have been reported. This paper gives the results obtained with other ionic solutions especially those containing ions with covalent linkages in them such as nitrates, sulphates, chlorates, bromates, iodates, etc. Amongst the substances that have been studied are 13 halides, 13 nitrates, 8 sulphates, 5 hydroxides, 9 chlorates, bromates and iodates, of monovalent and divalent elements. From the measured values of the Faraday effect and dispersion in these solutions the magneto-optic anomaly has been evaluated. The ionic rotations have also been computed. The last part of the paper gives the values of the magneto-optic anomaly of gases and vapours calculated from data obtained from Landolt and Bornstein's tables.

## 2. RESULTS

The magnetic rotation of the different solutions were measured for $\lambda 5461$ (Hg green) with water as the standard substance. The refractive indices were measured for $\lambda 5893$, $\lambda 5461$ and $\lambda 4358$. The experimental methods used have already been described in the previous communications by the author. The specific rotations of the ions in solutions are evaluated from the simple Verdet rule for mixtures.

$$[V_s] = [V_i]x_1 + [V_w]x_2,$$

where $[V_s]$, $[V_i]$ and $[V_w]$ are the specific rotation of the solution, ions in solution and water and $x_1$ and $x_2$ are the number of grams of the substance and water *in* 100 *grams of the solution.* The specific rotation $[V] = V/d$, where V is the Verdet constant and $d$ is the density and the molecular rotation $[V]_m = [V] \times M$ where M is the molecular weight. The magneto-optic anomaly for any solution is calculated from the modified Becquerel formula

$$V = \gamma\, e/2mc^2.\ (\lambda\, dn/d\lambda),$$

where $dn/d\lambda$ is the dispersion for the solution for the wavelength $\lambda$ for which the Verdet constant is measured. The solutions were made from purest chemicals. Some of the compounds were prepared in the laboratory. Usually a 4-molar solution was made. Table I gives the optical and magneto-optic constants of water and the other solutions. M is the molecular weight $X_1$ and $X_2$ are the number of grams of substance and water *in* 100 *c.c. of solution*, $d$ is the density, $n$ the refractive index and $\Delta n$ is $n_{5893}$-$n_{4358}$, $V_{5461}$ is the Verdet constant for the solution for $\lambda_{5461}$, $[V_i]_M$ is the molecular rotation of the ions in solution and $\gamma$ is the magneto-optic anomaly.

TABLE I

*Optical and magneto-optic constants for water*

| $n_{5893}$ | $n_{5461}$ | $n_{4358}$ | $\Delta n \times 10^5$ | $V_{5461}$ | $100\gamma$ |
|---|---|---|---|---|---|
| 1·33239 | 1·33381 | 1·33953 | 714 | 0·01547′ | 76 |

TABLE II

*The optical and magneto-optic constants of univalent nitrates in solution (4-Normal solution)*

| | M | $X_1$ | $X_2$ | $d$ | $n_{5893}$ | $\Delta n \times 10^5$ | $V_{5461} \times 10^3$ | $[V_i]_M \times 10$ | $100\gamma$ |
|---|---|---|---|---|---|---|---|---|---|
| $HNO_3$ .. | 63·02 | 25·26 | 83·20 | 1·0841 | * | 895 | 13·60′ | 2·10′ | 53·3 |
| $LiNO_3$ .. | 68·95 | 27·60 | 88·42 | 1·1600 | 1·35626 | 887 | 14·81′ | 2·85′ | 58·6 |
| $NaNO_3$ .. | 85·01 | 34·00 | 84·94 | 1·1814 | 1·36543 | 867 | 14·62′ | 3·70′ | 59·2 |
| $KNO_3$ .. | 101·11 | 40·48 | 80·83 | 1·2127 | 1·36621 | 871 | 14·40′ | 4·75′ | 58·0 |
| $NH_4NO_3$ | 80·05 | 32·02 | 81·44 | 1·1346 | 1·36811 | 883 | 15·10′ | 6·30′ | 60·0 |
| $AgNO_3$ | 169·89 | 68·00 | 84·39 | 1·5234 | 1·39832 | 1065 | 16·94′ | 9·60′ | 55·8 |

* Absolute value of $n$ was not determined accurately.

TABLE III

*The optical and magneto-optic constants of sulphates in solution* (1 *Normal*)

| | M | $X_1$ | $X_2$ | $d$ | $n_{5893}$ | $\Delta n \times 10^5$ | $V_{5461} \times 10^3$ | $[V_i]_M \times 10$ | $100\gamma$ |
|---|---|---|---|---|---|---|---|---|---|
| $H_2SO_4$ .. | 98·07 | 9·80 | 93·90 | 1·0370 | * | 775 | 15·10′ | 5·80′ | 69·2 |
| $Li_2SO_4$ .. | 109·94 | 11·00 | 93·02 | 1·0402 | 1·35056 | 745 | 15·13′ | 7·41′ | 71·3 |
| $Na_2SO_4$.. | 142·06 | 14·20 | 92·81 | 1·0662 | 1·35114 | 748 | 15·26′ | 9·07′ | 71·6 |
| $K_2SO_4$ .. | 174·26 | 17·50 | 89·16 | 1·0658 | 1·35144 | 756 | 14·91′ | 11·22′ | 69·2 |
| $(NH_4)_2SO_4$ | 132·14 | 13·20 | 90·50 | 1·0371 | 1·35600 | 781 | 15·43′ | 14·37′ | 69·3 |

* Absolute value of $n$ was not determined accurately.

TABLE IV

*The optical and magneto-optic constants of hydroxides* (4 *Normal*)

| | M | $X_1$ | $X_2$ | $d$ | $n_{5893}$ | $\Delta n \times 10^5$ | $V_{5461} \times 10^3$ | $[V_i]_M \times 10$ | $100\gamma$ |
|---|---|---|---|---|---|---|---|---|---|
| HOH .. | 18·02 | .. | .. | 1·0000 | 1·33239 | 715 | 15·47′ | 2·78′ | 76 |
| LiOH .. | 23·95 | 9·58 | 97·74 | 1·0732 | 1·36691 | 788 | 17·32′ | 5·50′ | 77 |
| NaOH .. | 40·00 | 16·00 | 95·57 | 1·1157 | 1·36770 | 792 | 17·43′ | 6·65′ | 77 |
| KOH .. | 56·11 | 22·44 | 90·96 | 1·1340 | 1·36816 | 796 | 17·08′ | 7·52′ | 76·8 |
| $NH_4OH$* | 35·05 | 3·50 | 15·66 | 0·9917 | 1·33503 | 730 | 15·66′ | 8·60′ | 76·3 |

* 1 Normal solution.

TABLE V

*The optical and magneto-optic constants of chlorates*

| | M | $X_1$ | $X_2$ | $d$ | $n_{5893}$ | $\Delta n \times 10^5$ | $V_{5461} \times 10^3$ | $[V_i]_M \times 10$ | $100\gamma$ |
|---|---|---|---|---|---|---|---|---|---|
| $HClO_3$ .. | 84·47 | 33·78 | 82·02 | 1·1580 | 1·36780 | 813 | 15·85′ | 7·92′ | 68·4 |
| $LiClO_3$ .. | 90·40 | 36·36 | 82·58 | 1·1894 | 1·36820 | 798 | 16·36′ | 8·93′ | 72·0 |
| $NaClO_3$ .. | 106·30 | 42·52 | 82·92 | 1·2544 | 1·36880 | 790 | 16·56′ | 9·32′ | 73·6 |

## TABLE VI

*The optical and magneto-optic constants of bromates and iodates*

| | M | $X_1$ | $X_2$ | $d$ | $n_{5893}$ | $\Delta n \times 10^5$ | $V_{5461} \times 10^3$ | $[V_i]_M \times 10$ | $100\gamma$ |
|---|---|---|---|---|---|---|---|---|---|
| $HBrO_3$ .. | 128·93 | 38·67 | 77·67 | 1·1634 | .. | 880 | 16·65′ | 15·46′ | 67·0 |
| $NaBrO_3$.. | 150·92 | 45·27 | 86·74 | 1·3201 | .. | 890 | 18·58′ | 17·18′ | 73·3 |
| $HIO_3$ .. | 175·93 | 52·77 | 88·61 | 1·4138 | 1·40150 | 1051 | 22·61′ | 29·75′ | 75·5 |
| $LiIO_3$ .. | 181·86 | 54·54 | 89·04 | 1·4358 | 1·40367 | 1008 | 21·69′ | 26·41′ | 75·5 |

## TABLE VII

*The optical and magneto-optic constants of divalent chlorides*

| | M | $X_1$ | $X_2$ | $d$ | $n_{5893}$ | $\Delta n \times 10^5$ | $V_{5461} \times 10^3$ | $[V_i]_M \times 10$ | $100\gamma$ |
|---|---|---|---|---|---|---|---|---|---|
| $CaCl_2$ .. | 111·0 | 44·4 | 78·68 | 1·2308 | † | 852 | 20·85′ | 26·27′ | 85·9 |
| $SrCl_2$ .. | 158·55 | 63·42 | 63·19 | 1·2661 | 1·38549 | 920 | 20·14′ | 27·30′ | 76·8 |
| $BaCl_2$*.. | 208·28 | 62·46 | 62·14 | 1·2460 | 1·37643 | 842 | 19·04′ | 30·70′ | 79·4 |
| $MgCl_2$ .. | 95·24 | 38·09 | 76·61 | 1·1470 | 1·37751 | 892 | 19·80′ | 25·00′ | 78·0 |
| $ZnCl_2$ .. | 136·30 | 54·52 | 66·96 | 1·2148 | 1·39251 | 933 | 20·13′ | 27·80′ | 75·7 |
| $CdCl_2$ .. | 183·33 | 73·33 | 57·10 | 1·3043 | 1·39963 | 951 | 20·92′ | 32·10′ | 77·4 |

* 3 Normal solution. † Accurate value not determined.

## TABLE VIII

*Magneto-optic constants of divalent bromides*

| | M | $X_1$ | $V_{5461} \times 10^3$ | $[V_i]_M \times 10$ | $100\gamma$ |
|---|---|---|---|---|---|
| $CaBr_2$ .. | 199·91 | 79·96 | 31·22 | 48·6′ | 75·2 |
| $SrBr_2$ .. | 247·46 | 98·98 | 31·71′ | 49·7′ | 76·0 |
| $MgBr_2$ .. | 184·15 | 73·66 | 30·84′ | 46·1′ | 74·4 |
| $ZnBr_2$ .. | 225·21 | 90·00 | 32·00′ | 49·6′ | 77·0 |
| $CdBr_2$ .. | 272·24 | 108·00 | 33·70′ | 53·7′ | 77·9 |

TABLE IX

*Magneto-optic constants of divalent iodides*

| | M | $X_1$ | $V_{5461} \times 10^3$ | $[V_i]_M \times 10$ | 100γ |
|---|---|---|---|---|---|
| $ZnI_2$ .. | 319·2 | 95·76 | 32·03′ | 102·27′ | 67·8 |
| $CdI_2$ .. | 366·2 | 109·86 | 29·06′ | 106·43′ | 68·3 |

TABLE X

*Magneto-optic constants of divalent nitrates* (4 *Molar solution*)

| | $X_1$ | $V_{5461} \times 10^3$ | $[V_i]_M \times 10$ | 100γ |
|---|---|---|---|---|
| $Ca(NO_3)_2$ .. | 65·64 | 13·46 | 5·80′ | 43·0 |
| $Sr(NO_3)_2$ .. | 84·66 | 13·80′ | 6·81′ | 43·3 |
| $Ba(NO_3)_2$* .. | 26·13 | 15·24′ | 10·21′ | 65·1 |
| $Mg(NO_3)_2$ .. | 59·33 | 12·96′ | 4·16′ | 43·2 |
| $Zn(NO_3)_2$ .. | 75·76 | 14·37′ | 7·03′ | 44·4 |
| $Cd(NO_3)_2$ .. | 94·95 | 16·21′ | 11·04′ | 48·7 |
| $Pb(NO_3)_2$ .. | 66·24 | 19·81′ | 33·00′ | 50·3 |

* 2 Molar Solution.

TABLE XI

*Molecular magnetic rotation of substances*

| Substance | $[V_i]_M \times 10$ |
|---|---|
| NaF .. | 2·20′ |
| KF .. | 3·24′ |
| $NH_4F$ .. | 4·71′ |
| $MgSO_4$ .. | 5·40′ |
| $ZnSO_4$ .. | 8·20′ |
| $CdSO_4$ .. | 11·90′ |
| $HgCl_2$ .. | 37·58′ |
| $HgI_2$* .. | 129·84′ |
| $Mg(BrO_3)_2$ .. | 35·87′ |
| $Zn(BrO_3)_2$ .. | 37·82′ |

* Pyridine Solution.

### 3. Discussion of Results

Tables XII and XIII give the difference between the molecular magnetic rotation of different compounds. One notices that the additivity rule is fairly valid. From these tables the ionic rotations have been computed (Table XIV) assuming that the rotation for the hydrogen ion is zero. This is only strictly true if the hydrogen ions in solution consist of free protons. The metal ions have much smaller rotation than the acid ions. Tables XV and XVI give the values of the magneto-optic anomaly for all the solutions for which measurements have been made so far. It must be mentioned here that the $\gamma$ value for water is 0·76.

It has been reported in a previous paper that the $\gamma$ values of free ions having the inert gas configuration is very nearly unity and that any deviation of the electron atmospheres from the inert gas state is immediately indicated by the decrease of the anomaly. In the case of ions with strong covalent linkages the electron atmosphere would have considerably departed from the inert gas state and consequently on the basis of the above observation the $\gamma$ value in such ions should be extremely low. This is found to be so in the

**Table XII**

*Molecular Rotation*

(In minutes × 10)

| | H | Li | Na | K | $NH_4$ | Ca | Sr | Mg | Zn | Cd |
|---|---|---|---|---|---|---|---|---|---|---|
| Cl–F .. | .. | .. | 12·30 | 12·20 | 12·00 | .. | .. | .. | .. | .. |
| Br–Cl .. | 11·49 | 11·42 | 11·27 | 11·36 | 11·52 | 11·16 | 11·20 | 10·50 | 10·91 | 10·8 |
| I–Cl .. | 36·79 | 37·90 | 38·54 | 39·51 | 39·45 | .. | .. | .. | .. | .. |

**Table XIII**

*Molecular Rotation*

(In minutes × 10)

| | Cl | Br | I | $NO_3$ | OH | $ClO_3$ | $\frac{1}{2}SO_4$ |
|---|---|---|---|---|---|---|---|
| Li–H .. | 0·59 | 0·42 | 1·60 | 0·75 | (2·72) | 1·01 | 0·80 |
| Na–Li .. | 1·40 | 1·30 | 2·04 | 0·85 | 1·15 | 0·43 | 0·83 |
| K–Li .. | 2·35 | 2·29 | 3·96 | 1·95 | 2·02 | .. | 1·91 |
| $NH_4$–Li .. | 3·62 | 3·72 | 5·23 | 3·45 | 3·10 | .. | 3·47 |

TABLE XIV

*Ionic Rotations*

(In minutes × 10)

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| H | — | Ca | 1·35 | F | 0·60 | $ClO_3$ | 7·92 | $NO_3$ | 2·10 |
| Li | 0·60 | Sr | 2·38 | Cl | 12·41 | $BrO_3$ | 15·46 | $SO_4$ | 2·90 |
| Na | 1·72 | Ba | 5·88 | Br | 24·10 | $IO_3$ | 29·75 | OH | ·90 |
| K | 2·70 | Mg | ε | I | 49·40 | | | | |
| Rb | 4·09 | Zn | 2·80 | | | | | | |
| Cs | 7·21 | Cd | 6·84 | | | | | | |
| $NH_4$ | 4·15 | Hg | 12·66 | | | | | | |

case of nitrates, sulphates, chlorates, bromates and iodates (Tables XV and XVI). Further it must be remembered that each of these substances contains at least one metal ion for which $\gamma = 1$. The value of the anomaly for the acid radicals (in $NO_3$, $SO_4$, $ClO_3$, $BrO_3$, $IO_3$) must therefore be considerably lower than the values given in Tables XV and XVI. These figures seem to lend very good support to the idea that the presence of covalent bond decreases the value of $\gamma$ of a substance. If this were true then the anomaly should be lowest in the groups that contain the strongest covalent bonds.

TABLE XV

*Magneto-optic anomaly of* 4 *Normal solutions*

| | H | Li | Na | K | $NH_4$ |
|---|---|---|---|---|---|
| Cl | 77·8 | 79·6 | 81·4 | 81·1 | 79·6 |
| Br | 79·5 | 81·1 | 84·3 | 83·1 | 83·4 |
| I | 79·8 | 82·9 | 83·4 | 85·1 | 84·7 |
| $NO_3$ | 53·3 | 58·6 | 59·2 | 58·0 | 60·0 |
| ½ $SO_4$* | 69·2 | 71·3 | 71·6 | 69·2 | 69·3 |
| OH | 76·0 | 77·0 | 77·0 | 76·8 | 76·3 |
| $ClO_3$ | 68·4 | 72·0 | 73·6 | .. | .. |
| $BrO_3$ | 67·0 | .. | 73·3 | .. | .. |
| $IO_3$ | 75·5 | 75·5 | .. | .. | .. |

* 2 Molar solution.

TABLE XVI

$100\gamma$ (4 *Molar solutions*)

| | Ca | Sr | Ba | Mg | Zn | Cd |
|---|---|---|---|---|---|---|
| $Cl_2$ .. | 85·9 | 76·8 | 79·4 | 78·0 | 75·7 | 77·4 |
| $Br_2$ .. | 75·2 | 76·2 | .. | 74·4 | 77·0 | 77·9 |
| $I_2$ .. | .. | .. | .. | .. | 67·8 | 68·3 |
| $(NO_3)_2$ .. | 43·0 | 43·3 | 65·1 | 43·2 | 44·4 | 48·7 |

An idea of the strengths of these bonds can be obtained from certain Raman frequencies of these groups. Table XVII gives the Raman frequency (Hertzberg, 1946) and the force constants as also the values of the anomaly for 4 Normal solutions of salts containing these ions. One notices that the ions that have the greatest frequency, *i.e.*, the strongest binding have the least value of $\gamma$ when dissolved in water.

TABLE XVII

| Ion | $100\gamma$ of 4 normal solution | Raman frequency $cm.^{-1}$ | Force const. $k \times 10^5$ dynes /cm. |
|---|---|---|---|
| $NO_3$ .. | 58 | 1050 | 10·39 |
| $SO_4$ .. | 64 | 981 | 9·07 |
| $ClO_3$ .. | 73 | 930 | 5·55 |
| $BrO_3$ .. | 74 | 806 | 5·25 |
| $IO_3$ .. | 75 | 779 | 5·35 |

The anomaly for pure acids are given in Table XVIII. The low values are most probably due to the covalent linkages that exist in these acids in the pure state. The solutions of the acids in water have a much higher value of the anomaly.

TABLE XVIII

| Acid | $100\gamma$ |
|---|---|
| $HNO_3$ .. | 20·0 |
| $H_2SO_4$ .. | 42·4 |
| HBr .. | 38·0 |
| HCl .. | 62·0 |

The divalent halides of Zn and Cd which are known not to dissociate completely in water have low values of the anomaly. The ammonium salt solutions have a lower value of $\gamma$ than the corresponding alkali salt solutions probably due to the covalent N-H bond.

### 4. Magneto-Optic Anomaly in Gases and Vapours

The studies in ionic solutions indicate that there is a relationship between the strength of binding and the magneto-optic anomaly of a molecule. It was therefore thought worthwhile to collect together the values of the anomaly of gases and vapours and to find whether there is any similar relationship there also. Darwin and Watson (1928) have calculated the anomaly in the case of only five gases $O_2$, $H_2$, $N_2$, $CO_2$ and $N_2O$. In the case of other gases and vapours there are measurements of the Faraday effect for one or two wavelengths in the visible region (Landolt & Bornstein Tables). The dispersions of the gases were also obtained from the same source and the values of the anomaly have been calculated. Table XIX gives the value of $\gamma$ of the different gases and vapours.

Table XIX

| Gas | Neon | Argon | $H_2$ | HCl | $H_2S$ | HBr | $H_2O$ |
|---|---|---|---|---|---|---|---|
| 100$\gamma$ | 116·5 | 100 | 99 | 92·8 | 89·8 | 80·8 | 78 |
| Gas | $SO_2$ | $Cl_2$ | CO | $N_2$ | $CO_2$ | $(CN)_2$ | ($N_2O$) |
| 100$\gamma$ | 72·5 | 70·7 | 65·6 | 63·0 | 53·7 | 48·1 | 32·0 |

| Gas | $C_2H_2$ | $C_2H_4$ | $C_2H_6$ | $C_3H_8$ | $CH_3Cl$ |
|---|---|---|---|---|---|
| 100$\gamma$ | 66·7 | 61·2 | 60·1 | 58·0 | 48·3 |

| Gas | $CHCl_3$ | $C_2H_5Br$ | $CCl_4$ | $CS_2$ |
|---|---|---|---|---|
| 100$\gamma$ | 70·1 | 77·4 | 60·4 | 36·0 |

The anomaly in most gases and vapours range from 0·32 to 1·00. The high value of 1·16 in the case of neon is probably due to experimental errors. The $\gamma$ value of argon is almost exactly the theoretical value of unity. The lower value of the constant found in the other gases must obviously be due to the failure of Larmor's theorem in molecules. Unfortunately the determination of the ratio of the angular momentum of an electron to its magnetic moment in a molecule is a very complicated process and has been accomplished and that too approximately, in the case of the hydrogen molecule (Van Vleck, 1932). It would be of some interest to find out whether there is any relation-

ship between the magneto-optic anomaly and the valence force constant of a molecule. The values of the force constant can be calculated directly from data on Raman and infra-red spectra. Table XX gives the values of $\gamma$ and the force constants for all the gases for which data are available.

TABLE XX

| Gas | Force constant $\times 10^5$ dynes/cm. | $100\gamma$ |
|---|---|---|
| $(CN)_2$ .. | 17·73 | 48·2 |
| $CO_2$ .. | 16·8 | 54 |
| CO .. | 11·82 | 65 |
| $SO_2$ .. | 9·97 | 72 |
| $H_2O$ .. | 7·76 | 78 |
| HBr .. | 4·00 | 81 |
| $H_2S$ .. | 4·14 | 90 |
| HCl .. | 5·15 | 93 |
| $H_2$ .. | 4·99 | 99 |
| $CS_2$ .. | 8·1 | 36 |
| $CCl_4$ .. | 4·38 | 60 |

From Table XX one can see that the anomaly is very intimately connected with the strength of binding, stronger the binding, the lower is the anomaly. (There are of course many discrepancies, *e.g.*, HBr, $CS_2$,$CCl_4$, etc.) On this basis it is possible to understand why the value of $CH_3Cl$ ($\gamma = 0{\cdot}48$) is lower than that for $CHCl_3$ ($\gamma = 0{\cdot}70$). The stretching force constant for = C–H is $4{\cdot}79 \times 10^5$ dynes/cm. while that for C–Cl is only $3{\cdot}64 \times 10^5$ dynes/cm. and the latter compound contains more C–Cl bonds than the former. But on this basis it is impossible to explain the intermediate value of $\gamma = 0{\cdot}60$ for $CCl_4$. The extremely low value of 0·36 for $CS_2$ does not also find an explanation on this basis.

The author wishes to record his grateful thanks to Prof. R. S. Krishnan for his kind encouragement during these investigations.

## SUMMARY

The paper records the magneto-optic rotation and the dispersion for a large number of ionic solutions. From these data the magneto-optic anomaly for these solutions have been evaluated. The ionic rotation for the different substances have also been estimated. Amongst the substances studied are halides, nitrates, sulphates, hydroxides, chlorates, bromates and iodates of monovalent and divalent elements. The anomaly in some pure acids have also been determined. The magneto-optic anomaly for about twenty-three gases and vapours have been calculated from the data given in Landolt and Bornstein's tables. It is found that the presence of

ions with covalent linkages decreases the value of the anomaly for water, the decrease being greater if the strength of the covalent bond is greater. In the case of gases also the value of the anomaly is lower for gases in which the strength of the bonds is greater. There are some vapours that do not follow this rule.

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# CHEMOTHERAPY OF TUBERCULOSIS

## Part V. Synthesis of Some $N^4$-Acyl-$N^1$-Aryl Sulphanilhydroxamides

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Of the numerous derivatives of sulphanilamide which have exhibited marked activity in experimental chemotherapy but have however not received adequate attention since their synthesis, the $N^4$-acyl sulphanilhydroxamides constitute an interesting group. The first members of this group were synthesised by Kharasch and Reinmuth[1] and, more extensively, by Moore, Miller and Miller.[2] Among the large number of homologous $N^4$-acyl sulphanilhydroxamides, the $N^4$-*n*-butyryl-, $N^4$-*n*-valeryl-, $N^4$-*n*-hexanoyl-, $N^4$-*n*-heptanoyl-, and $N^4$-*n*-octanoyl sulphanilhydroxamides were found to be more effective antistreptococcal agents than sulphanilhydroxamide, sulphanilamide or sulphapyridine,[2, 3, 4] while the toxicity of the active members was greatly below that of sulphanilamide. Hampil, *et al.* (*loc. cit.*) also found these compounds to be effective against meningococci. More recently, Goldfarb[5] synthesised $N^1$-*o*-methyl-, and $N^1$-*o*-benzyl sulphanilhydroxamides and found their bacteriostatic activities to be midway between those of sulphanilamide and sulphathiazole as expected on the basis of their pKa values in accordance with the Bell-Roblin theory.[6] One of the most promising member of this series, $N^4$-*n*-caproylsulphanilhydroxamide or "sulphabenamide", has been studied at some length by Hansen and Kreidler[7] who confirmed its therapeutic usefulness in $\beta$-hæmolytic streptococcal infections of rabbits.

The hope that the sulphanilhydroxamides may be of some value in the chemotherapy of mycobacterial infections was stimulated by an announcement by Gubner[8] that sulphabenamide was definitely beneficial in human tuberculosis. Gubner reported that five cases of advanced bilateral pulmonary tuberculosis, treated over ten months, gave absence of the tubercle bacilli from sputum and disappearance of the lesions. He also stated that no toxic effects developed when the drug was administered in quantities upto an ounce in 16 hours, or when given over a period of 10 months. However, sulphabenamide was pronounced too toxic by Smith and McClosky[9] on the basis of their chemotherapeutic studies in experimental guinea-pig tuberculosis. Another interesting feature about the $N^4$-acyl

sulphahydroxamides was their relative instability reported by Moore, *et al.* (*loc.cit.*) who stated that these compounds slowly dissolved at room temperature in dilute alkali with evolution of a gas and a formation of $N^4$-acylaminobenzenesulphinic acids. While assessing the antimycobacterial potentialities of the $N^4$-acyl sulphanilhydroxamides and ascertaining their exact mode of chemotherapeutic action, it was considered profitable to pay particular attention to $N^4$-acyl-$N^1$-substituted sulphanilhydroxamides which were expected to be more stable than those already available. Accordingly, the synthesis of $N^4$-acyl-$N^1$-aryl or heterocyclic sulphanilhydroxamides were undertaken. So far, only the preparation of a series of $N^4$-acyl-$N^1$-(mono- or dichloro-) phenyl sulphanilhydroxamides has been completed. The halogenated derivatives were especially attractive in view of the possibility of these being unantagonised by *p*-aminobenzoic acid similar to other halogenated sulphonamides recently disclosed.[10] The compounds synthesised are presented in the table.

The $N^4$-acyl-$N^1$-substituted sulphanilhydroxamides were obtained by the reaction of suitable $N^4$-acylsulphanilyl chlorides on freshly prepared specimens of the requisite halogenated $\beta$-phenylhydroxamides in pyridine medium.

*Substituted Sulphonamidohydroxamides*

| Serial No. | Name of the Compound | Molecular Formula | M.P./°C. | Nitrogen percentage | |
|---|---|---|---|---|---|
| | | | | Found | Required |
| 105 | $N^4$-*n*-Butyrylsulphanil-$\beta$-3-chlorophenyl hydroxamide | $C_{16}H_{17}O_4N_2SCl$ | 210–14 | 7·6 | 7·6 |
| 106 | $N^4$-*n*-Valerylsulphanil-$\beta$-3-chlorophenyl hydroxamide | $C_{17}H_{19}O_4N_2SCl$ | 195–97 | 7·6 | 7·3 |
| 107 | $N^4$-*n*-Caproylsulphanil-$\beta$-3-chlorophenyl hydroxamide | $C_{18}H_{21}O_4N_2SCl$ | 187–90 | 7·5 | 7·6 |
| 108 | $N^4$-*n*-Butyrylsulphanil-$\beta$-4-chlorophenyl hydroxamide | $C_{16}H_{17}O_4N_2SCl$ | 157–59 | 7·3 | 7·6 |
| 109 | $N^4$-*n*-Valerylsulphanil-$\beta$-4-chlorophenyl hydroxamide | $C_{17}H_{19}O_4N_2SCl$ | 216–17 | 7·3 | 7·3 |
| 110 | $N^4$-*n*-Caproylsulphanil-$\beta$-4-chlorophenyl hydroxamide | $C_{18}H_{21}O_4N_2SCl$ | 212–14 | 7·8 | 7·6 |
| 111 | $N^4$-*n*-Butyrylsulphanil-$\beta$-2:5-dichlorophenyl hydroxamide | $C_{16}H_{16}O_4N_2SCl_2$ | 143–44 | 6·7 | 7·0 |
| 112 | $N^4$-*n*-Valerylsulphanil-$\beta$-2:5-dichlorophenyl hydroxamide | $C_{17}H_{18}O_4N_2SCl_2$ | 140–42 | 6·9 | 7·0 |
| 113 | $N^4$-*n*-Caproylsulphanil-$\beta$-2:5-dichlorophenyl hydroxamide | $C_{18}H_{20}O_4N_2SCl_2$ | 141–42 | 6·8 | 7·0 |
| 114 | $N^4$-*n*-Butyrylsulphanil-$\beta$-3:4-dichlorophenyl hydroxamide | $C_{16}H_{16}O_4N_2SCl_2$ | 139–40 | 6·9 | 7·0 |
| 115 | $N^4$-*n*-Valerylsulphanil-$\beta$-3:4-dichlorophenyl hydroxamide | $C_{17}H_{18}O_4N_2SCl_2$ | 135–36 | 6·7 | 7·0 |

## EXPERIMENTAL

The simple substituted β-phenylhydroxylamines needed in this investigation were prepared by a further modification of the elegant method of Lapworth and his co-workers[11] based on the original preparative procedure of Willstatter and Kubli for β-phenylhydroxylamines.

The general procedure used for the synthesis of substituted β-phenylhydroxylamines is exemplified in the preparation of 4-chloro-β-phenylhydroxylamine.

*4-Chloro-β-phenylhydroxylamine.*—The reagent used for the reduction was prepared by adding drop by drop concentrated hydrochloric acid (105 c.c.) to a solution of anhydrous sodium sulphide (150 g.) dissolved in water (325 c.c.) with the aid of long dropping funnel, the lower end of which reaching to the bottom of the solution. This reagent was transferred to a glass stoppered bottle containing *p*-chloronitrobenzene (65 g.), toluene (75 c.c.) and a saturated solution of calcium chloride (50 g.). The mixture was shaken up vigorously for about one and a half hour to cause an emulsion keeping the temperature below 30° C. by occasional cooling. As the reduction proceeded liquid became thicker and the colour gradually darkened to deep orange. The reduction was completed in approximately two to two and a half hours and then ammonium chloride (60 g.) was added and the mixture was shaken to dissolve the inorganic matter. The precipitate of crystalline 4-chloro-β-phenylhydroxylamine was filtered, washed with water and finally with petroleum ether. The product thus obtained was crystallised from dilute alcohol, yield 42 g.

The substituted β-phenylhydroxylamines synthesised are tabulated as follows:—

| Compound | Formula | M.P./°C. | Yield % | Nitrogen percent. | |
|---|---|---|---|---|---|
| | | | | Found | Required |
| 3-Chloro-β-phenyl hydroxylamine | $C_6H_6ONCl$ | 98–100 | 60 | 9·73 | 9·75 |
| 4-Chloro-β-phenyl hydroxylamine | $C_6H_6ONCl$ | 99–100 | 55 | .. | .. |
| 2:4 Dichloro-β-phenylhydroxylamine | $C_6H_6ONCl_2$ | 77–78 | 70 | 7·7 | 7·9 |
| 3:4-Dichloro-β-phenylhydroxylamine | $C_6H_5ONCl_2$ | 135–37 | 30 | 5·7<br>5·65<br>(unstable) | 7·9 |

The N-acyl sulphanilyl chlorides used in these experiments were obtained by the methods already available in literature.[12, 13] The earlier workers had used the crude sulphochlorides on the ground that these were not very stable. It was now found to be advantageous to utilise in the present condensations stable acyl sulphanilyl chlorides which resulted by crystallisation from dilute acetone (charcoal).

We express our grateful thanks to Major-General Sir Sahib Singh Sokhey, Director, Haffkine Institute, Bombay, and Dr. K. Ganapathi, for their kind interest in these investigations. We are also thankful to Mr. M. H. Shah, B.Sc., for carrying out all the analyses.

## Summary

A series of sulphanilamides derived from N-carbo and heterocyclic hydroxamides have been synthesised, since a number of $N^4$-acyl sulphanilhydroxamides have been favourably reported on in preliminary experimental bacterial infections. Among the latter was *sulphabenamide* or $N^4$-caproyl sulphanylhydroxamide, which was said to be effective clinically in streptococcal infections and tuberculosis. This is a new class of sulphanilamides involving the preliminary synthesis of some hitherto unknown substituted aryl- and heterocyclic hydroxamides. The compounds of this series so far prepared are the $N^4$-*n*-butyryl-, the $N^4$-*n*-valeryl-, and the $N^4$-*n*-caproyl-sulphanilyl derivatives of $\beta$-3-chlorophenyl-, $\beta$-4-chlorophenyl-, $\beta$-2:5-dichlorophenyl-, and $\beta$-3:4-dichlorophenyl-hydroxylamines.

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# A MODIFIED METHOD FOR ESTERIFICATION OF SOME POLYHYDROXY AROMATIC ACIDS

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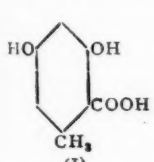
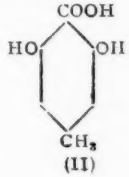
The most general method for esterification is the catalytic method due to Fischer and Speier.[1] The esterification can also be carried out with alkyl sulphates or alkyl iodides using alkali hydroxides or carbonates in presence of suitable anhydrous solvents. In case of hydroxybenzoic acids however, it is likely that this method may simultaneously lead to partial etherification also. The Fischer-Speier method also fails in case of some polyhydroxy benzoic acids. Thus *o*-orsellinic acid has been esterified only by the diazomethane method;[2] its ethyl and higher esters have been obtained from natural sources.[3] *p*-Orsellinic acid has been esterified by diazomethane and also by the action of methyl and ethyl iodides on its silver salt.[4] The usual catalytic method fails in these cases probably due to steric hindrance or due to the ease of decarboxylation of these acids which may be occurring due to the temperature of the reaction or the presence of the acid.

As the esters of *o*- and *p*-orsellinic acids (I and II) were required for some synthetical work, various possible methods for their esterification were investigated. During the course of the investigation, it was observed that esterification could successfully be carried out by refluxing the acid for about 10 hours in a dry medium like acetone with an alkyl halide (3 mols.) or dialkyl sulphate (1·25 mols.) in presence of a neutral substance like sodium bicarbonate (1·25 mols.).

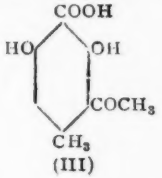
Excellent yields of methyl esters (80%) were obtained by this method on esterification of *o*- and *p*-orsellinic acids, with dimethyl sulphate and sodium bicarbonate. Sodium bicarbonate could be replaced by potassium bicarbonate without affecting the results. The use of potassium carbonate, however, resulted in poor yields. Replacements of dimethyl sulphate with methyl iodide diminished the yield (50-60%). The ethyl esters were obtained in 60-65% yield using either ethyl iodide or diethyl sulphate.



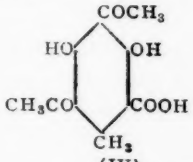
(I)



(II)



(III)



(IV)

To explore its general applicability, this method was applied to prepare methyl and ethyl esters of α- and β-resorcylic acids, phloroglucinol carboxylic acid, benzoic acid, 3-acetyl-*p*-orsellinic acid (III) and 3 : 5-diacetyl-*o*-orsellinic acid (IV). α- and β-resorcylic acids and phloroglucinol carboxylic acid on esterification with dimethyl sulphate gave good yields (60-70%) of the corresponding ester. Comparative less yields were obtained of the ethyl esters. During the esterification of phloroglucinol carboxylic acid, decarboxylation was sometimes found to take place. In some cases, replacing of sodium by potassium bicarbonate did not give satisfactory results. Benzoic acid also gave poor yields (20%) and most of the benzoic acid was recovered unchanged. This is rather surprising, as there being no hydroxyl group present, benzoic acid would ordinarily be expected to give better yields. It appears, therefore, that better yields are obtained by this method with polyhydroxybenzoic acids probably because of their stronger acidic nature.

Esterification was also carried out of 3-acetyl-*p*-orsellinic acid and 3 : 5-diacetyl-*o*-orsellinic acid, products obtained only in small quantities during the course of some other synthetical work, when 60-90% yields of the esters were obtained.

Experiments were conducted with *p*-orsellinic acid and β-resorcylic acid using good excess of dimethyl sulphate and sodium bicarbonate (2·5 mols· each) to see whether the hydroxy group is attacked. However no methyl ether could be isolated thus showing that excess of these reagents does not lead to etherification of the hydroxy groups in hydroxy benzoic acids.

This new method of esterification has several advantages and would be useful for some acids like polyhydroxybenzoic acids for which catalytic method cannot be used. Other advantages are that the reactions are carried out under mild conditions in absence of any strong acidity or alkalinity. It is a good substitute for the diazomethane method and has an advantage over it that it is simpler and that esters higher than the methyl can also be prepared and there is no chance of etherification of a hydroxyl group, if present. Moreover, it has been found to give good results even on working with small amounts of the acid.

## Experimental

### *General method of esterification*

The acid was dissolved in acetone (dried over anhydrous potassium carbonate) and refluxed with alkali bicarbonate (1·25 mols.) and dialkyl sulphate (1·25 mols.) or alkyl halide (3 mols.) for about 10 hours. The reaction mixture filtered and the residue washed with acetone. The filtrate and the washing were mixed and acetone removed. The crude product was

| No. | Acid | Alkylating agent | | Alkaline reagent | | Ester | | Remarks |
|---|---|---|---|---|---|---|---|---|
| | | Name | Mols. | Name | Mols. | Yield | m.p. | |
| | | | | | | g. | C. | |
| 1 | *p*-Orsellinic acid[4] (m.p. 166–67°) | $Me_2SO_4$ | 1·25 | $NaHCO_3$ | 1·25 | 1·6 | 99°[2] | 0·1 g. of acid recovered |
| 2 | do | do | 2·5 | do | 2·5 | 1·6 | 99° | do |
| 3 | do | do | 1·25 | $KHCO_3$ | 1·25 | 1·6 | 99° | .. |
| 4 | do | MeI | 3·0 | $NaHCO_3$ | 1·25 | 0·8 | 97–99° | 0·8 g. of acid recovered |
| 5 | do | $Et_2SO_4$ | 1·25 | do | 1·25 | 1·2 | 61°[4,5] | 0·8 g. of acid recovered |
| 6 | do | do | 1·25 | $KHCO_3$ | 1·25 | 1·2 | .. | .. |
| 7 | do | EtI | 3·0 | $NaHCO_3$ | 1·25 | 1·3 | 61° | 0·2 g. of acid recovered |
| 8 | do | do | 3·0 | $KHCO_3$ | 1·25 | 1·3 | .. | .. |
| 9 | do | do | 3·0 | $K_2CO_3$ | 1·0 | 0·8 | 61° | Crude yield contaminated with potassium salt of acids |
| 10 | *o*-Orsellinic acid[6] (m.p. 178°) | $Me_2SO_4$ | 1·25 | $NaHCO_3$ | 1·25 | 1·6 | 138–39°[2] | .. |
| 11 | do | MeI | 3·0 | do | 1·25 | 1·2 | 138° | .. |
| 12 | do | $Et_2SO_4$ | 1·25 | do | 1·25 | 1·2 | 132°[7] | .. |
| 13 | do | EtI | 3·0 | do | 1·25 | 1·2 | 132° | .. |
| 14 | β-Resorcylic acid[8] (m.p. 213–17°) | $Me_2SO_4$ | 1·25 | $NaHCO_3$ | 1·25 | 1·4 | 188°[9] | .. |
| 15 | do | do | 2·5 | do | 2·5 | 1·4 | 188° | .. |
| 16 | α-Resorcylic acid[10] (m.p. 232–34°) | do | 1·25 | $NaHCO_3$ | 1·25 | 1·0—1·2 | 161–64°[11] | .. |
| 17 | Phloroglucinol carboxylic acid[12] (100° decomp.) | do | 1·25 | $NaHCO_3$ | 1·25 | 1·0 | 176–77°[13] | 0·2 g. of acid recovered |
| 18 | do | do | 1·25 | $KHCO_3$ | 1·25 | 1·0 | 176–77° | Crude product contaminated with potassium salt of the acid |
| 19 | do | $Et_2SO_4$ | 1·25 | $NaHCO_3$ | 1·25 | 0·4 | 123–24°[14] | 0·5 g. of acid recovered |
| 20 | do | do | 1·25 | $KHCO_3$ | 1·25 | 0·1 | 123° | Crude product consisted mostly of potassium salt of the acid |
| 21 | do | EtI | 3·0 | $NaHCO_3$ | 1·25 | 0·1 | 123° | 1·2 g. of acid recovered |
| 22 | do | do | 3·0 | $KHCO_3$ | 1·25 | .. | .. | 0·3 g. of acid and 0·7 g. of phloroglucinol |
| 23 | Benzoic acid .. | $Me_2SO_4$ | 1·25 | $NaHCO_3$ | 1·25 | 0·4 | b.p. 195–200°[15] | 1·0 g. benzoic acid recovered |
| 24 | 3-Acetyl-*p*-orsellinic acid (m.p. 170°)* | do | 1·25 | do | 1·25 | 0·075 | 94–95°* | 0·1 g. of the acid was used for esterification |
| 25 | 3:5-Diacetyl-*o*-orsellinic acid* (m.p. 151°) | do | 1·25 | $NaHCO_3$ | 1·25 | 0·05 | 99–100°* | do |
| 26 | do | $Et_2SO_4$ | 1·25 | do | 1·25 | .. | 96–97°* | do |

* The products marked with an asterisk are unkown and are described in the following paper.

washed first with sodium bicarbonate solution and then with water, when the ester was obtained usually in a fairly pure state. It was further purified by crystallisation.

The results of the experiments carried out under various conditions are given in the table. In all the cases 2·0 g. of the acid was used except in Nos. 24, 25 and 26 where the esterification was carried out with 0·1 g. of the substance. The m.p. of all the known esters were found to agree with those recorded in literature.

## Summary

A new method of esterification of acids is described. In this method the esterification is carried out in a dry medium (acetone) in presence of neutral substance like sodium or potassium bicarbonate with alkyl halide or alkyl sulphate. Yields of methyl esters varying from 50-80% are obtained on esterification of *o*- and *p*-orsellinic acids, α- and β-resorcylic acids, phloroglucinol carboxylic acid, 3-acetyl-*p*-orsellinic acid and 3 : 5-diacetyl-*o*-orsellinic acid. However, only 25% yield of methyl benzoate was obtained from benzoic acid.

This new method has several advantages. It would be particularly useful for some acids like polyhydroxybenzoic acids in which the catalytic method cannot be used, and would be a good substitute for the diazomethane method as it is simpler and also as esters higher than methyl can be prepared, there being no chance of etherification of a hydroxyl group, if present. Good results are obtained on esterification of even small amounts of the acid.

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# SODA METASOMATISM IN THE FERRUGINOUS QUARTZITES OF THE BABABUDAN HILLS, MYSORE STATE

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The presence of amphiboles like bababudanite and cummingtonite in the banded ferruginous quartzites of the Bababudan Hills has long been known. The ferruginous quartzites were considered in earlier years, to have been formed by the alterations of rocks containing such amphiboles (W. F. Smeeth, 1908, p. 213; P. Sampat Iyengar, 1908, p. 73).

It was shown, however, in 1933, that the occurrence of bababudanite was confined to narrow zones in the immediate vicinity of igneous intrusives (C. S. Pichamuthu and M. R. Srinivasa Rao, 1933, pp. 276–77). The mineral was quite fresh and often developed right across the bands in the ferruginous quartzites, which indicated that it was formed after the ironstones had attained their banded nature.

Intercalated with the ferruginous quartzites, there occur layers of bababudanite-magnetite schists which are often only an inch or two in thickness, and impersistent. Glistening crystals of the amphibole are found in a matrix composed of magnetite and granoblastic quartz. These schists were also considered to have had a similar contact metamorphic origin (C. S. Pichamuthu, 1935 *a*, p. 608).

During the course of the writer's examination of the Bababudans, a yellowish or brownish green pyroxene was also found sometimes in these contact zones (C. S. Pichamuthu, 1935 *b*, pp. 21–22). The chemical and optical properties of this mineral indicate that it is a soda-bearing pyroxene similar to ægirine.

Table I gives the chemical composition of these soda-bearing minerals and schist. It will be seen from this that bababudanite contains 8·8 per cent. of $Na_2O$, the soda-pyroxene 9·7 per cent., and the bababudanite-magnetite schist 2·6 per cent. The basic rocks adjoining and underlying the banded ferruginous quartzites of the Bababudan Hills are many of them rich in soda, as may be seen from the prevalence of albite and acid oligoclase, and the writer was therefore disposed to ascribe the source of soda to the sediments being derived from these spilitic rocks, the formation of the soda-bearing minerals being facilitated by the contact metamorphic action of the igneous intrusions (C. S. Pichamuthu, 1936, pp. 43–44).

TABLE I

| | Bababudanite | Soda-pyroxene | Bababudanite-magnetite schist |
|---|---|---|---|
| $SiO_2$ .. | 49·80 | 52·75 | 44·15 |
| $Al_2O_3$ .. | 1·56 | 0·35 | 0·25 |
| $Fe_2O_3$ .. | 18·62 | 33·00 | 40·20 |
| FeO .. | 10·59 | 1·42 | 7·98 |
| MgO .. | 9·30 | 0·24 | 3·11 |
| CaO .. | 0·45 | 0·80 | tr |
| $Na_2O$ .. | 8·80 | 9·70 | 2·60 |
| $K_2O$ .. | tr | tr | tr |
| $H_2O^+$ .. | 0·65 | 1·00 | 0·05 |
| $H_2O^-$ .. | | 0·50 | 1·60 |
| $TiO_2$ .. | .. | .. | tr |
| $P_2O_5$ .. | .. | tr | tr |
| Total .. | 99·77 | 99·76 | 99·94 |

Bababudanite .. .. Kemmangandi, Bababudan Hills, Mysore.
*Analyst:* W. H. Herdsman, Glasgow.

Soda-pyroxene .. .. Kalhatti, Bababudan Hills, Mysore.
*Analyst:* W. H. Herdsman.

Bababudanite-magnetite schist .. Bababudan Hills, Mysore.
*Analyst:* W. H. Herdsman.

Similar explanations have been given for the development of soda-amphibles in the ferruginous quartzites of South Africa (P. A. Wagner, 1928, p. 72; A. L. Hall, 1925, p. 135). The crocidolite found in those banded ironstones contains soda varying from 3·9 per cent. to 7·71 per cent. Both Peacock (1928, pp. 271–72) and Hall (1930, p. 252) considered the soda to be original and dependent upon special conditions of deposition resulting in soda-rich bands in the ironstones.

According to this explanation, the necessary soda must be disseminated throughout the banded ferruginous quartzites or concentrated in certain layers, but it is difficult to understand such distribution and the form in which soda would be present in these rocks. In order to determine whether the banded ferruginous quartzites of the Bababudans contained soda, the writer recently got two typical specimens of these rocks analysed by Mr. B. S. Raju, Chemist of the Mysore Geological Department. One of these was a hæmatite quartzite from Virupakshikan, and the other a magnetite quartzite from near Hebbe. Both these specimens contained no trace of soda. The iron ores derived from the ferruginous quartzites near Kalhatti also do not contain any soda.

Sills and dykes of albite quartz dolerite (now epidioritised) have invaded the Bababudan formations, and the soda-bearing minerals have developed in the banded ferruginous quartzites only in the immediate vicinity of these

igneous intrusives. The residual solutions expelled from this basic rock must have been sufficiently sodic to bring about the formation of these amphiboles and pyroxenes in the neighbouring ironstones. This area, therefore, affords a good example of the metasomatic transference of soda from a basic igneous to a sedimentary rock.

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# STUDIES ON NIOBIUM AND TANTALUM

## Part I. Tartratoniobic Acid

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### Introduction

The weak acids formed from the amphoteric elements, vanadium, niobium and tantalum combine readily with organic hydroxy acids to give soluble complexes. It is known that melts of niobic and tantalic acids in potassium hydrogen sulphate are soluble in solutions of oxalic and tartaric acids and also in ammonium salt solutions of these organic acids. Freshly precipitated niobic acid dissolves in solutions of oxalic and tartaric acids resulting in the formation of complex compounds. Russ (1902) prepared nioboxalic acid and investigated its properties; Edmister and Albritton (1932) furnished evidence for the formation of tartracolumbic acid. While the oxalato complexes of niobium have been studied in some detail, the tartrato complexes have not received much attention. Hence a systematic study of the tartrato compounds was undertaken and the preparation and properties of tartratoniobic acid are described in this paper.

### Experimental

*Purity of materials*

The starting material for the preparation and study of the compounds of niobium was purified potassium niobium fluoride $K_2NbF_7$. This was decomposed with sulphuric acid in a platinum dish, and stirred with water, when a thick white precipitate of niobic acid was thrown down. It was collected, washed with hot water and finally by an ammoniacal solution of ammonium chloride and filtered. The niobic acid was dried and ignited strongly in a platinum dish at 800° C. in an electric muffle furnace. To eliminate any final traces of sulphuric acid, the ignited niobium pentoxide was mixed with ammonium carbonate and again ignited at 800° C. for 5 hours. The niobium pentoxide thus prepared was a perfectly white shining powder. The purity of the pentoxide was tested by the procedure as outlined by Schoeller (1937); Titanium was estimated colorimetrically, using hydrogen peroxide after Pierre Sue (1937). Tantalum pentoxide was determined by

the modified procedure of Krishnaswami and Suryanarayana Murthy (1935). In the sample of the niobium pentoxide, combined water, alkali metals, sulphide-forming metals and iron were absent. Silica 0·08% and titanium dioxide 0·46% were present. Therefore the purity of niobium pentoxide was 99·46%. All materials used in this work were very pure. *d*-Tartaric acid, melting point 169° C. was used.

*Preparation*

The preparation of this tartrato complex has been set out in a preliminary note by the author (1947). The dissolving action of tartaric acid on niobic acid differs depending on the conditions of formation and reaction of the niobic acid. It was found that niobic acid which was precipitated by a mineral acid either from a lixiviated melt of potassium hydrogen sulphate or potassium carbonate with the earth acid, was not soluble in tartaric acid solution. The method finally adopted to prepare the tartratoniobic acid is outlined below:—Ignited niobium pentoxide was fused with potassium hydrogen sulphate in a silica crucible as recommended by Powell (1925). The melt was extracted with a saturated solution of ammonium oxalate, filtered and diluted to nearly thrice its volume. The solution was brought to boiling and ammonia added cautiously and with continuous stirring till there was a slight excess of the reagent. A copious white precipitate was formed and when a saturated solution of ammonium chloride was added, the fine heavy precipitate settled down quickly. The precipitate was filtered and washed with hot water and it was observed that filtration was slow; moreover if considerable time elapsed between precipitation and treatment with tartaric acid, the solubility of the precipitate in tartaric acid was adversely affected. Therefore the precipitate was washed by centrifuging, till it was free from ammonia as tested by Nessler's reagent. The washed precipitate was suspended in 10% tartaric acid, heated over the water-bath for 3 hours and let stand overnight. The undissolved precipitate was centrifuged and separated. The clear supernatant solution, that was obtained, when tested was found to contain niobic acid. The solution was concentrated on a water-bath to about half the volume. The thick solution that resulted was kept over calcium chloride in a desiccator for two days. The volume was further reduced by half but no solid was found to separate. Crystallisation was not brought about even when the solution was cooled in freezing mixture. Finally, in order to isolate the solid from the solution, a few ml. of alcohol was added drop by drop with vigorous stirring. A white substance was thrown down instantaneously; it was filtered under gentle suction, washed with alcohol and dried in air. The alcoholic filtrate was

found to contain only tartaric acid. The substance appeared to be microcrystalline and contained niobium and tartaric acid. A method was devised for its analysis.

*Analysis*

(1) *Niobium.*—The substance was dissolved in water, the solution was heated to boiling and concentrated hydrochloric acid added drop by drop with vigorous stirring. A white precipitate of niobic acid was obtained which settled down quickly. The precipitation of niobium was found to be quantitative. The precipitate was allowed to stand for 1 hour, filtered, and washed till free of chlorine ions. The washsed precipitate was dried, ignited strongly, cooled and weighed finally as $Nb_2O_5$.

(2) *Tartaric Acid.*—Tartaric acid, in the filtrate from the hydrochloric acid precipitation, was determined by the Goldenberg (1908) method.

(3) *$H_2O$.*—The water content was computed by difference and dehydration in air and in vacuum was also done.

*Result*

TABLE I

| | Found % | $Nb_2O_5 \cdot (C_4H_4O_5)_2 \cdot 10H_2O$% |
|---|---|---|
| $Nb_2O_5$ .. | 37·36 | 37·44 |
| $C_4H_4O_5$ .. | 37·10 | 37·20 |
| $H_2O$ .. | 25·54 | 25·36 |

The experimental results agree very closely with the theorectical values and hence the compound prepared can be represented by the formula $Nb_2O_5(C_4H_4O_5)_2 \cdot 10\ H_2O$ and can be named as 2-tartrato-2-niobic acid 10-hydrate in accordance with the rules for naming inorganic compounds of the International Union of Chemistry (Jorissen, *et al.*, 1940).

*Recrystallisation*

Large quantities of this substance were prepared with a view to recrystallising from water. The substance was dissolved in warm water to a concentrated solution and allowed to cool. Since there was no separation of crystals, the solution was chilled in a freezing mixture for nearly two hours with seeding. No crystals separated. The solution was kept over concentrated sulphuric acid; as the volume became less, the solution became thick and viscous. Complete evaporation resulted in a cake-like mass. Therefore

resort was taken to crystallisation with the aid of alcohol. The crystals got were analysed as described previously. The following results wre obtained.

TABLE II

| | Found % |
|---|---|
| $Nb_2O_5$ .. | 37·21 |
| $C_4H_4O_5$ .. | 37·05 |
| $H_2O$ .. | 25·74 |

The results agreed closely with those obtained earlier as shown in Table I and show that the substance can be recrystallised from water with the aid of alcohol without change.

*Properties*

2-Tartrato-2-niobic acid is a light straw coloured substance. It is very soluble in water, the solubility at 0° C. being 6·49 g./100 g. water. Its aqueous solution can be kept for a long time without decompositon by the carbon dioxide of the atmosphere. It is acidic to methyl orange. Alkali hydroxides and ammonia do not precipitate niobia from its solution. All mineral acids and acetic acid decompose it with the precipitation of niobic acid, which is quantitative unlike the case of nioboxalic acid. Tannin imparts a red colour to the solution and a scarlet red precipitate is formed with the addition of a mineral acid, owing to the formation of an adsorption complex. It is insoluble in ether, while some heteropoly acids are known to be ether soluble. It precipitates albumen as heavy white threads. Its aqueous solution when boiled for a long time, undergoes hydrolytic decomposition with the formation of another soluble complex compound. Examination of the substance under polarising microscope revealed that the substance was crystalline in nature, the crystals being very tiny.

*Electrical Conductivity*

The conductivity of tartratoniobic acid solutions was measured in a cylindrical type of cell of pyrex glass with a ground glass stopper. The platinum electrodes were freshly coated with platinum black. The Kohlrausch method was used for measuring conductivity of solutions at 25° C., by taking the usual precautions. The conductivity was followed with change in dilution. Molecular conductivity was calculated assuming the molecular weight to be 354·9. The results are shown in the accompanying table.

TABLE III

| No. | Dilution | Specific conductivity | Molecular conductivity |
|---|---|---|---|
| 1 | M/10 | $5{\cdot}0944\times10^{-3}$ | 50·94 |
| 2 | M/20 | $3{\cdot}0044\times10^{-3}$ | 60·05 |
| 3 | M/40 | $1{\cdot}7714\times10^{-3}$ | 70·85 |
| 4 | M/80 | $1{\cdot}0014\times10^{-3}$ | 80·08 |
| 5 | M/160 | $5{\cdot}4684\times10^{-4}$ | 87·48 |
| 6 | M/320 | $3{\cdot}1324\times10^{-4}$ | 100·20 |
| 7 | M/640 | $1{\cdot}7544\times10^{-4}$ | 112·30 |
| 8 | M/1280 | $9{\cdot}4340\times10^{-5}$ | 120·80 |
| 9 | M/2560 | $5{\cdot}6950\times10^{-5}$ | 145·80 |
| 10 | M/5120 | $3{\cdot}0250\times10^{-5}$ | 154·90 |
| 11 | M/10240 | $1{\cdot}8220\times10^{-5}$ | 186·60 |
| 12 | M/20480 | $1{\cdot}1490\times10^{-5}$ | 235·20 |
| 13 | M/40960 | $6{\cdot}8430\times10^{-6}$ | 280·20 |
| 14 | M/81920 | $4{\cdot}0150\times10^{-6}$ | 328·80 |

The conductivity of the sodium salt of this acid was determined with a view to arrive at the basicity of the acid by Ostwald's rule. Exactly M/32 and M/1024 solutions were prepared and their conductivities were determined at 25° in the cell described above. The basicity was calculated and found to be 7·1.

*Molecular weight.*—The molecular weight of tartratoniobic acid was determined by measuring the depression in freezing point in water by the Beckmann method. The standard apparatus was used with all the usual precautions, the special feature of the apparatus being a platinum stirrer operated by an electromagnet. The results are summarised in Table IV.

TABLE IV

| No. | Tartratoniobic acid g. | Depression △° | Molecular weight |
|---|---|---|---|
| 1 | 0·6681 | 0·138<br>0·139 | 360·3<br>357·7 |
| 2 | 0·9350 | 0·194<br>0·198<br>0·199 | 358·6<br>351·3<br>349·6 |
| 3 | 1·5498 | 0·318<br>0·328 | 362·4<br>351·3 |
| | Average .. | | 355·9 |

*pH measurements.*—In order to find out the strength of the 2-tartrato-2-niobic acid prepared, pH measurements were made by using the quinhydrone

electrode under standard conditions. The pH of 0·1 molar and 0·05 molar solutions were found out

| Molarity | pH. |
|---|---|
| 0·1 | 3·34 |
| 0·05 | 3·41 |

It is seen that the tartratoniobic acid is much stronger than niobic acid from which the complex acid is formed: this is a characteristic property of heteropoly acids.

*Optical rotation.*—It is known from a study of the complex compounds of molybdenum, tungsten, etc., with tartaric acid that the optical rotation is enhanced considerably in the tartrato complexes. To find out whether there was any enhancement in optical rotation in the tartratoniobic acid prepared, measurements of rotation were made with different concentrations of solutions in a polarimeter in the usual way. The following table summarises the results.

TABLE V

| Con. of Soln. % | $\alpha_D^{28°}$ | $[\alpha]_D^{25°}$ | $[M]_D^{25°}$ |
|---|---|---|---|
| 4 | +0·61 | 15·25 | 5440 |
| 2 | +0·5 | 25·00 | 8870 |
| 1 | +0·31 | 31·00 | 12005 |

By comparing the values for molecular rotations of tartratoniobic acid with those observed for the same concentrations of tartaric acid it is seen that the maximum enhancement in optical rotation has been nearly six times.

*Dehydration.*—The compound obtained in this work, *viz.*, tartratoniobic acid was dehydrated in air and in vacuum to find out the loss in water by the substance at different stages. Dehydration in air was carried out by heating the substance to constant weight in an air-oven maintained at different temperatures. When the substance was heated for 2 hours, the equilibrium value for drying could be attained. Subsequent heating at the same temperature changed the weight very little. Since the substance tended to become brown and decompose above 150° C. they were heated to a maximum of 135° C to avoid decomposition of the compound.

Dehydration in vacuum was carried out in a specially designed apparatus (see diagram). The technique employed was as follows:

A weighed amount of the substance was taken in the tube and fixed to the joint with high vacuum grease. The stop-cock $T_1$ was kept closed. With

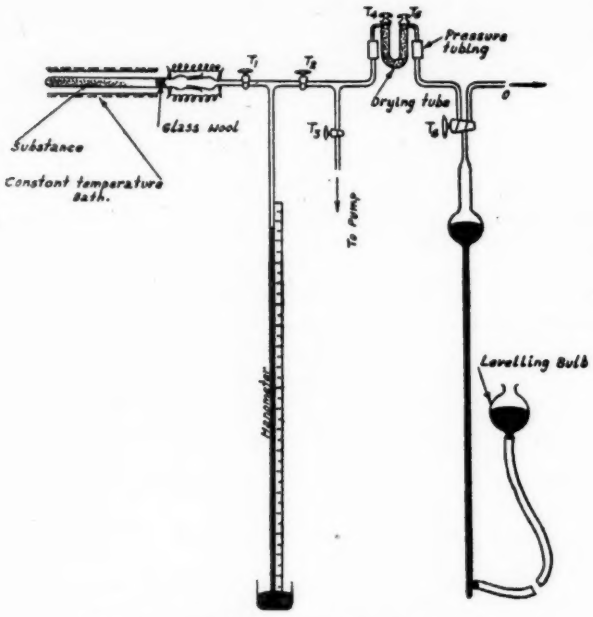


FIG. 1. Apparatus for the Study of Dehdration

$T_6$ kept closed, the system was evacuated through $T_3$ with a Cenco Hyvac pump and $T_3$ closed. The substance was not directly exposed since this would entail a loss of water during evacuation. The air in the tube containing the substance was topplered out through the outlet O. Very good vacuum was obtained. $T_1$, $T_2$, $T_4$ and $T_5$ were closed. The U-tube containing $P_2O_5$ was disconnected and wieghed. It was again put in place and the space between $T_1$ and $T_6$ evacuated. The substance was exposed to $P_2O_5$ and allowed to remain usually for 3 hours, at that temperature though the absorption of water by the desiccant was over in about 30 minutes. The stop-cocks were closed, the U-tube was taken out and the gain in weight determined. The substance was maintained at fixed temperatures by using vapour baths, *viz.*, acetone 53° C·, water 98° C., and xylene 135° C. The water removed at each temperature was determined. Finally the tube with the dehydrated substance was also weighed to check up with the gain in weight of the U-tube.

2-*Tartrato*-2-*niobic acid*.$Nb_2O_5 \cdot (C_4H_4O_5)_2 \cdot 10\ H_2O$.—Dehydration in air for this substance was conducted as outlined above at 3 temperatures and the results are recorded below in Table VI.

TABLE VI

| Temp. °C. | $H_2O$ lost % | Molecules of $H_2O$ Removed | Molecules of $H_2O$ Retained |
|---|---|---|---|
| 50 | 0·39 | 0·15 | 9·85 |
| 110 | 5·76 | 2·27 | 7·73 |
| 130 | 7·68 | 4·03 | 6·97 |

In vacuum the dehydration was conducted at 4 temperatures and the following results were obtained.

TABLE VII

| Temp. °C. | $H_2O$ lost % | Molecules of $H_2O$ Removed | Molecules of $H_2O$ Retained |
|---|---|---|---|
| 25 | 1·455 | 0·574 | 9·426 |
| 53 | 5·215 | 2·056 | 7·944 |
| 98 | 8·725 | 3·440 | 6·560 |
| 135 | 10·446 | 4·120 | 5·880 |

It can be seen from Tables VI and VII that 2-tartrato-2-niobic acid loses 3 molecules of water by heating to 130° C in air; in vacuum at 135° C. one more molecule of water is capable of being removed while the other six molecules of water are more firmly bound and cannot be easily removed.

## DISCUSSION

When niobic acid was reacted with tartaric acid, a complex compound of the formula $Nb_2O_5 \cdot (C_4H_4O_5)_2 \cdot 10 \cdot H_2O$ was formed which had been isolated. The reaction and properties of this compound can be explained on the assumption of a heteropoly acid structure to this tartratoniobic acid. The most satisfactory theory for the structure of heteropoly acids is due to Miolati (1908) and this is based on Werner's conception of co-ordination compounds. This theory was further developed by Rosenheim and Janecke (1917). According to Miolati-Rosenheim theory, niobium, the central atom or nucleus, should always be hydrated to six atoms of oxygen. If so, the compund $H_7NbO_6$ should be taken as the parent acid in solution, which can be derived from metaniobic acid as follows:

$HNbO_3\ 3H_2O \rightarrow H_7NbO_6$. In this hydrated niobic acid, the oxygen atoms are replaced by tartrate radicals. If there has been replacement of one oxygen atom by one tartrate radical, the following equation will hold good:—

$$H_7NbO_6 + C_4H_6O_6 \rightarrow H_7\left[Nb\begin{matrix}O_5\\(C_4H_4O_6)\end{matrix}\right] + H_2O.$$

On this basis, the tartratoniobic acid that has been prepared can be represented as $H_7\left[Nb\begin{matrix}O_5\\(C_4H_4O_6)\end{matrix}\right]1{\cdot}5\,H_2O$.

On the contrary, if the tartrate radical is assumed to occupy two co-ordination positions in the complex, then the constitution of the complex should be represented as

$$H_5\left[Nb\begin{matrix}O_4\\(C_4H_4O_6)\end{matrix}\right]2{\cdot}5\,H_2O.$$

The compound is unsaturated and even in presence of considerable excess of tartaaric acid, no other compound more saturated than the one prepared is formed.

It has been observed that it is difficult to obtain crystals of tartratoniobic acid from aqueous solutions, and resort had to be taken to the use of alcohol. Russ (1902) has similar difficulties in isolating nioboxalic acid. Edmister and Albritton (1932) report that they obtained crystals of tartracolumbic acid of the formula (Nb (OH) $(C_4H_4O_6)_2$ by aqueous crystallisation; however, the compound was precipitated from solution by acetone. In the case of the tartratoniobic acid prepared' it is found that its aqueous solution becomes easily supersaturated and there is no tendency to crystallise. It is common with the tartrato complexes of many metals to exhibit this phenomenon. This also finds a parallel in the observations on supersaturated solutions of tartaric acid. Taimmi (1928) has stated that in supersaturated solutions of tartaric acid, there is no tendency to crystallise spontaneously. Schweizer (1933) noticed that stable supersaturated solutions of tartaric acid even when cooled to $-192°$ for 6 hours yield only a glass and no crystals on melting, though inoculation with crystal nucleii gives some crystals. Thus tartratoniobic acid solution also becomes easily supersaturated and hence the difficulty of growing crystals from its solution.

It has been seen that in 2-tartrato-2-niobic acid, the optical rotation is enhanced sixfold. This finds a parallel in the cases of the tartrate compelxes of molybdenum and tungsten, in which complex formation increases the optical rotation several fold. Gernez (1887, 1888) states that sodium molybdate in the proportion of $Na_2MoO_4$ to 2 $C_4H_6O_6$ increases the rotation 37 times while one molecule of ammonium molybdate increases the rotation of three molecules of tartaric acid 56 times. Sodium tungstate, increases the rotation 22 times. Mallemann (1921) found that the addition of $H_3BO_4$, $H_3SbO_4$, $H_2MoO_4$ and $H_2WO_4$ to aqueous solutions of *d*-tartaric acid gave compounds with high rotatory power. Cordier and Murgier (1941)

who studied the optical rotation of solutions of sodium tungstate and tartaric acid found that a complex of the formula $WO_3 \cdot C_4H_6O_6$ was formed whose rotation was 15-30 times that of tartaric acid alone. Thus it is evident that niobic acid also behaves in a similar way by yielding a higher order tartrato compound with enhanced rotation and the cause of the enhancement may be attributed to the phenomenon of dynamic isomerism.

The 2-tartrato-2-niobic acid is strongly acidic as indicated by the pH measurements. It is much stronger than the corresponding nuclear acid, niobic acid, which is only comparable in strength to silicic acid as reported by Weinland and Storz (1907). In this behaviour the tartratoniobic acid conforms to the work of Abegg and Bodlander (1899) who have shown that the complex acid is always stronger than the nuclear acid. This principle can be illustrated by the example of arsenic, provided by Rosenheim and Traube (1915), where it is found that the compound $H_3$ [AS $(Mo\ O_4)_3O$] is much stronger than $H_3ASO_4$. Thus the heteropoly acids are always stronger than their nuclear acids and niobium follows the general rule.

Even a dilute solution of tartratoniobic acid throws down a curdy white precipitate from albumen solutions which is a characteristic reaction of heteropoly acids.

The basicity of the heteropoly acids is not easily determined. In the case of the 2-tartrato-2-niobic acid, Ostwald's basicity rule has been made use of, which gives a value of 7 for the acid. If this value of 7 is accepted, it woud give a formula $H_7\left[Nb\begin{matrix}O_5\\(C_4H_4O_6)\end{matrix}\right] 1{\cdot}5\ H_2O$ for the acid prepared, *viz.*, $Nb_2O_5 \cdot (C_4H_4O_5)_2 \cdot 10\ H_2O$. This formula at once suggests that there are seven replaceable hydrogen atoms, which can be replaced by metals. However, it has been experimentally realised that in the alkali salts only one hydrogen atom is replaced by the alkali metal. Further such a compound would be expected to be highly ionised; but evidence got from molecular weight and conductivity data goes to show that the compounds are not highly ionised. The conductivity of salts with two ions at λ1024 is of the order of 130, while the conductivity of the sodium salt of tartratoniobic acid at λ1024 is 140·5. The acid also exhibits a similar conductivity. It must be pointed out here that in many heteropoly acids there are hydrogen atoms which can not be replaced by metal atoms but still exhibit an acidic reaction. These have been termed as "pseudoacidic". The view regarding the existence of 'pseudoacidic' hydrogen atoms is supported by the data obtained during the dehydration of the compound.

2-Tartrato-2-niobic acid $Nb_2O_5 \cdot (C_4H_4O_5)_2 \cdot 10H_2O \cdot$ retains 7 molecules of water and loses only 3 molecules by heating in air to 130° C. and further removal seems impossible. This would suggest that the last molecule of water left behind are in some way linked to the nuclear atom rendering removal difficult. Also according to the Miolati-Rosenheim theory, 3 molecules of water are hydrated to each central niobium atom which can be supposed to be retained firmly while the other molecules of water are held loosely and hence removed easily. The last molecules of water retained contribute the hydrogen atoms, which may be said to be ' pseudoacidic '.

The 2-tartrato-2-niobic acid 10-hydrate discussed above can be classified as a heteropoly acid. The following structure is suggested for it.

$$H_5\left[Nb\begin{matrix}O_4\\(C_4H_4O_6)\end{matrix}\right]2{\cdot}5\,H_2O.$$

## Summary

The formation of a higher order compound of niobium with tartaric acid has been investigated. Freshly precipitated niobic acid reacts with tartaric acid to yield a definite complex compound. The conditions of its formation have been studied. It analyses to the composition $Nb_2O_5 \cdot (C_4H_4O_5)_2 \cdot 10\,H_2O$. It is a light straw coloured substance and is very soluble in water. Its properties have been investigated. Its electrical conductivity has been determined at a series of dilutions and its basicity has been determined by the Ostwald method. Molecular weight of the compound has been found out by the cryoscopic method. The optical rotation of its solution shows an enhanced rotation. Dehydration conducted in air and in vacuum has revealed some features regarding its structure. According to the Rosenheim-Miolati theory, it is formulated as a heteropoly acid being derived from metaniobic acid $H_7NbO_6$ by the repacement of oxygen atoms by a tartrate radical and is represented as

$$H_5\left[Nb\begin{matrix}O_4\\(C_4H_4O_6)\end{matrix}\right]2{\cdot}5\,H_2O.$$

It is named as 2-tartrato-2-niobic acid 10-hydrate.

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